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Physical and Chemical Properties Division (838)

W.M. Haynes, Chief

A. Division Overview

1 Mission

The Physical and Chemical Properties Division serves as the Nation's reference laboratory for measurements, standards, data, and models in the areas of thermophysics, thermochemistry, and chemical kinetics. The Division focuses primarily on:

- thermophysical and thermochemical properties of gases, liquids, and solids, including both pure materials and mixtures;
- rates and mechanisms of chemical reactions in the gas and liquid phases;
- fluid-based physical processes and systems, including separations and low-temperature refrigeration and heat transfer.

The Division outputs include technical reports, Standard Reference Data, internet-based databases, calibrations, and Standard Reference Materials.

In order to carry out this Mission, the Division:

- develops, maintains, and utilizes advanced experimental tools and applies these to problems of scientific and industrial importance;
- compiles, evaluates, correlates, and interprets experimental data;
- develops and evaluates new theories, models, estimation methods, and computational algorithms;
- develops new dissemination mechanisms while maintaining a strong publication record in traditional media;
- carries out research leading to engineering data and models for advanced technologies;
- provides standards and services for fluid flow under cryogenic conditions;
- serves industry by organizing conferences, editing journals, training students, and serving on domestic and international committees.

1.1 Programs

The Physical and Chemical Properties Division is organized into six groups: (1) *Experimental Kinetics and Thermodynamics*; (2) *Chemical Reference Data and Modeling*; (3) *Computational Chemistry*; (4) *Experimental Properties of Fluids*; (5) *Theory and Modeling of Fluids*; and (6) *Cryogenic Technologies*. The last three Groups are located in Boulder, CO, as are three Projects, *Properties for Process Separations*, *Membrane Science and Technology*, and *Thermodynamics Research Center*. The rest of the Division is located in Gaithersburg, MD. These Groups/Projects are engaged in a number of research activities, which arise from several focus

areas that cut across Group/Project boundaries. These focus areas are discussed below, followed by selected Technical Highlights from these activities.

1.1.1 Basic Reference Data

Industry demands reliable and accessible reference data on the physical and chemical properties of a wide variety of compounds. These data are required in the development of models for process design, energy efficiency, and in the evaluation of possible environmental impacts. Basic reference data are also critical to the transportation and storage of fluids, in custody transfer, and for calibration of instruments and processes.

The development of databases for use in industry and academia is a fundamental task of all the focus areas within the Division. Thus, many of the Technical Highlights pertain both to Basic Reference Data and to a specific technical focus area. Several focused data activities of the Division are discussed in Technical Highlights 1-8, but this area permeates the discussion in nearly every report. The strong integration of data activities with the experimental, modeling, and computational programs means that experimental efforts often arise out of needs that these data activities identify. The integration of the Thermodynamic Research Center into NIST activities (Technical Highlight 3) reflects the growing demand for NIST properties data and the Division commitment toward fulfilling this demand. In Technical Highlight 9 we discuss an international conference that helps integrate and distill information on chemical reactions toward the development of new basic reference data and an understanding of the complex chemical processes involved.

- Kinetics Database on the Web (Technical Highlight 1)
- The NIST WebBook – NIST Chemical Reference Data for Industry (Technical Highlight 2)
- Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation (Technical Highlight 3)
- Standards for Calorimetry and Thermodynamics (Technical Highlight 4)
- International Cooperation on the Properties of Water and Aqueous Mixtures (Technical Highlight 5)
- Properties and Equations of State of Refrigerant Mixtures Near the Critical Point (Technical Highlight 6)
- Thermochemical and Chemical Kinetic Data for Organometallic Compounds (Technical Highlight 7)
- Thermal Decomposition of Chlorinated Alkanes: Testing the Evaluations (Technical Highlight 8)
- Fifth International Conference on Chemical Kinetics (Technical Highlight 9)

1.1.2 Computational Chemistry

The use of modern computational chemistry methodologies in the prediction of molecular properties has become increasingly important mainly due to significant improvements in algorithms and the availability of powerful computer resources. This is particularly true in the

area of thermochemistry, where researchers in industry perform *ab initio* quantum chemistry calculations on a routine basis. Progress in this area, however, is hampered by a lack of standards, comparisons, and simplified methodologies. In addition to this external need, the experimental projects within the Division benefit greatly from having a strong computational capability available. These considerations have led us to establish a computational chemistry focus area in the Division. This year, we have continued to make significant progress in the compilation, evaluation, and dissemination of information about computational techniques. The results of this project have led to the continued development of a computational chemistry comparison and benchmark database (Technical Highlight 10). Although the initial focus of this database was on thermochemistry and structure, it has been now expanded to include other properties such as transition state structures and energies for kinetics, dipole moments, and ionization energies. In addition, improved methodologies for calculating thermodynamic and kinetic parameters and predicting chemical reactions have been developed and applied to a variety of problems of interest in industry and in our own Division (Technical Highlights 11 and 12). Technical Highlight 13 describes the use of quantum Monte Carlo to estimate electronic excited states for chemical systems for which these states are important.

More recently, increasing interest in the semiconductor industry in rational design of materials leading to the manufacture of novel electronic components at the nanometer scale has prompted us to initiate a program studying the validation of state-of-the-art *ab initio* quantum chemical methodologies in the area of molecular electronics (Technical Highlight 14). Given that the nanofabrication of these materials will likely entail the use of self-assembly monolayers containing molecules interacting via long-range forces, it is important to have a fundamental understanding of the nature of these forces. Although quantum chemistry could offer the appropriate tools to achieve this goal, there is a significant lack of validation of these methodologies. We also continue to look into the validation of *ab initio* molecular orbital methodologies.

- Computational Chemistry Comparison and Benchmark Database (Technical Highlight 10)
- Development of Efficient Tools for Computational Kinetics (Technical Highlight 11)
- Software for Predicting Chemical Reactivity (Technical Highlight 12)
- Benchmark Reference Calculations of Excited State Transition Energies by Quantum Monte Carlo (Technical Highlight 13)
- Theoretical Studies of Electrical Conductance in Molecular Wires (Technical Highlight 14)

1.1.3 Fundamental Studies of Fluids

In support of the Division mission to provide U.S. industry with thermophysical properties of gases, liquids, and solids, the Division maintains a focus area on the fundamental studies of fluids, with strong experimental and theoretical components. The goals are to develop and utilize unique experimental, theoretical, and simulation capabilities to study fluid systems under equilibrium and nonequilibrium conditions. Much of the work relates to phase boundaries, vapor-liquid and solid-fluid equilibria, simulation of model systems, virial coefficients for mixtures, etc., including complex interactions associated with nanocomposites. In this area, we

both respond to current industrial needs and develop capabilities that anticipate future needs. Some of the areas of focus are:

- Virial Coefficients for Aqueous Systems (Technical Highlight 15)
- Solid-Fluid Equilibrium (Technical Highlight 16)
- Simulation of Viscous Properties of the Lennard-Jones Fluid (Technical Highlight 17)
- Microscale Heat Transfer (Technical Highlight 18)
- Workshop on Predicting the Thermophysical Properties of Fluids by Molecular Simulation (Technical Highlight 19)

Technical Highlight 19 describes a workshop that was organized by our division to identify industrial fluid property needs that could be addressed using molecular simulation methods and to ensure that industry has the tools necessary to employ molecular simulation methods as reliable options for the longer term. It is anticipated that the theoretical work, such as that related to solid-fluid equilibria, mixture virial coefficients, molecular simulation, etc., can lead to models upon which future data evaluation, prediction, and database efforts will be based. Some of our work on processes and structures at the micrometer and nanometer length scales may lead to broader programs in these areas to support industrial requirements as they are identified.

1.1.4

1.1.5 Tools for Chemical Analysis

Central to all of chemistry is the analysis of complex mixtures and the identification of the individual chemical constituents. These analyses are usually derived from basic physical/chemical properties of the species, and knowledge of these properties is thus critical to the reliability of the information. The Division strives to produce evaluated data, predictive algorithms, and analysis software to assist in the identification and quantitation of a range of species under diverse conditions. The NIST WebBook plays a central role in this, but current Division activities also include measurements and data acquisition designed to expand the gas chromatographic and mass spectrometric databases (Technical Highlight 20). Another important activity in the Division is the development of complex algorithms for the rapid and automatic analysis and deconvolution of GC/MS data for the identification of chemical-weapon agents (Technical Highlight 21).

- The NIST Spectral Database: Extending the Evaluation (Technical Highlight 20)
- Automated Gas Chromatography/Mass Spectral Decomposition and Analysis: Tools for Automating and Improving the Use of GC/MS Instruments (AMDIS) (Technical Highlight 21)

1.1.6

1.1.7 Cryogenic Technologies

Cryogenic technologies are critical to a wide variety of technically and industrially important areas. These include the cooling of infrared sensors for surveillance and atmospheric studies, the

cooling of superconducting electronics, magnets, and power systems, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas, and many other existing and potential applications. The research of the Division in this area involves the application of thermophysical concepts and measurements for temperatures below 120 K. Research in this area has focused primarily on improved measurement and modeling techniques involved in the development and characterization of novel and improved cryocoolers (Technical Report 23), studies of microscale heat transfer (Technical Report 18), development of a cryogenic materials database, and the maintenance and improvement of the national standard for cryogenic flow measurements. As part of an upgrade, the cryogenic flow loop has been brought into compliance with ISO Guide 25 requirements.

- Properties and Processes for Cryogenic Refrigeration (Technical Highlight 22)
- Microscale Heat Transfer (Technical Highlight 18)

2 Measurements for the Environment

The use of chemicals in American industry is ubiquitous and, thus, the fate and disposal of these industrial chemicals and their byproducts are of great concern. A wide variety of physical and chemical data are essential to understand the fate and impact of chemicals in the environment, to develop strategies for the removal or destruction of harmful byproducts, or to design processes and products that minimize environmental impact. A major consideration in the choice of chlorination chemistry as the first of our targeted evaluation projects (Technical Highlight 8) was the concern over the unintentional formation and release of chlorinated species in industrial processes. Our kinetics and thermodynamics databases have always been of particular importance in the development of environmental models and the needs of this community was a consideration in the new web-based kinetics database (Technical Highlight 1). The mass spectral database is a key tool in environmental analysis (Technical Highlight 20) and the tools we are developing for use in the decomposition and analysis of GC/MS data files will provide powerful new methods in that area (Technical Highlight 21). During the past year a new program was initiated on the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions (Technical Highlight 23). These Green ‘designer solvents’ that can serve as both catalyst and solvent are attracting increasing attention from industry since they promise significant environmental benefits.

2.1.1 In conjunction with our data activities, we have ongoing programs to generate key physical and chemical data for the environment. Our long-term program on the atmospheric degradation of industrial compounds has, in recent years, focused on halon replacements. This experimental activity has been closely tied to a computational effort, which has allowed us considerable leverage in providing needed information to industry and other agencies (Technical Highlights 11 and 24). Our experimental studies have involved the reactions of the hydroxyl radical with industrial gases in order to assess their potential environmental impact. Reactions of the hydroxyl radical in the gas phase are central to atmospheric chemistry and combustion processes. Our long-term effort to provide thermodynamic informa-

tion necessary for prediction of movement of heavy metals through ground waters (aquifers) and surface waters, and for prediction of remediation yields in treatment methodologies continues (Technical Highlight 25). During this past year work has focused on arsenic and chromium properties; both of these substances fall high on the 1999 CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) List of Priority Hazardous Substances. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a critical issue in a broad array of applications including pollution prevention and remediation (Technical Highlight 26). Our measurements on liquid systems will allow prediction of pollutant entry into ground waters. Studies also continue on the properties of electrolytes in aqueous and mixed solvents (important for waste-water and other environmental applications) (Technical Highlight 27).

- Exploring Reaction Kinetics and Physical Properties of Ionic Liquid Systems (Technical Highlight 23)
- Kinetics of Reactions of the Hydroxyl Radical (Technical Highlight 24)
- Thermodynamic Properties for Environmental Fate and Risk Evaluation: Arsenic and Chromium (Technical Highlight 25)
- Development of Efficient Tools for Computational Kinetics (Technical Highlight 11)
- Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes (Technical Highlight 26)
- Phase Equilibria Measurements and Models for Hazardous Chemical and Mixed Waste Systems (Technical Highlight 27)

2.1.2 Data for Process and Product Design

At some point in the manufacture of almost all the products that we use, there is a physical or chemical separation process involved. In modern industry, the products and processes are designed or optimized by process simulators. These rely on fundamental physical and chemical property data. The Division's goal is to provide the data that industry needs to effectively apply process modeling and simulation at all appropriate points in the manufacturing cycle, from the separation and treatment of raw feedstock, through the manufacturing process, to the ultimate treatment and disposal of waste streams. This has led to a wide variety of projects in the Division, some of which are strongly focused on a specific problem. Areas of current interest include:

- Measurements, Modeling, and Database Development for Supercritical Fluids and Alternative Solvents (Technical Highlight 28)
- Aircraft Fuel Tank Safety: An Application of Thermophysical Properties (Technical Highlight 29)
- Measurements and Data for Pressure-Driven Membrane Separations (Technical Highlight 30)

- Liquid, Vapor, and Gas Transport Properties in Membranes and Films (Technical Highlight 31)
- Properties and Processes for Cryogenic Refrigeration (Technical Highlight 22)

2.1.3 Properties of Energy-Related Fluids

Energy-related fluids include both those which are primary sources of energy – the fuels; and those which inter-convert heat and useful work – the working fluids. In several key areas, industry requires accurate and comprehensive equilibrium and transport property data and models for these fluids. These areas include the design and optimization of working cycles in refrigeration or power production systems; the design and control of gas processes; custody transfer; and development of new, cleaner energy systems. Efforts in the Division to meet these needs include the development of experimental apparatus for thermophysical property measurements; the acquisition of data; and the development and dissemination of accurate correlations. Recent work has focused on the thermophysical and transport properties of refrigerant mixtures near the critical point. An important facet of this focus area has been participation in the development of internationally accepted standards. Examples of activities under study in this focus area include:

- Properties and Equations of State of Refrigerant Mixtures Near the Critical Point (Technical Highlight 6)
- Chemistry and Properties of Trace Components in Fuel Gas (Technical Highlight 32)

Organizational Structure

Division-Office Projects (Gaithersburg and Boulder)

- Studies the behavior of fluid systems under both equilibrium and nonequilibrium conditions using unique experimental, theoretical, and simulation capabilities.

Properties for Process Separations Project (Boulder)

- Performs research and provides critically evaluated data and models on a variety of fluid-based separation processes, including distillation, adsorption, and supercritical fluid extraction.

2.1.3.1 Membrane Science and Technology Project (Boulder)

- Performs research on characterization techniques and provides fundamental data and models needed to design and/or select more efficient and robust materials for membrane-based separations.

Thermodynamics Research Center Project (Boulder)

- Collects, evaluates, and disseminates thermophysical property data for a very large number of fluid systems of interest to the chemical industry and related customers.

Experimental Kinetics and Thermodynamics Group (Gaithersburg)

- Develops and uses state-of-the-art measurement techniques to determine the rates and mechanisms of chemical reactions in the gas and liquid phases and the thermodynamic properties of industrially and environmentally important chemical species and materials.
- Develops new measurement methods for detecting and characterizing reactive intermediates.
- Certifies Standard Reference Materials for thermodynamic properties important to industry and science.

Chemical Reference Data and Modeling Group (Gaithersburg)

- Develops and evaluates new theories, models, and estimation methods for thermodynamic properties, rate constants, and molecular spectra.
- Compiles, evaluates, correlates, and disseminates Standard Reference Data.
- Develops and disseminates electronic databases and software on thermodynamics, chemical kinetics, and analytical mass and infrared spectra.

Computational Chemistry Group (Gaithersburg)

- Develops and applies computational methods for calculating the chemical and physical properties of selected species and systems.
- Critically compares computational predictions with the best available experimental data to establish the accuracy and reliability of computational methods.
- Develops resources to provide guidance to non-experts on methods, reliability, and resource requirements.

Experimental Properties of Fluids Group (Boulder)

- Performs experimental research and develops and maintains high-accuracy apparatus for measuring the full complement of thermodynamic and transport properties of fluids and fluids mixtures over wide ranges of temperature, pressure, and composition.
- Provides comprehensive thermophysical property measurements for technically important pure fluids and mixtures, including common organics and inorganics, hydrocarbons, refrigerants, and aqueous systems.

Theory and Modeling of Fluids Group (Boulder)

- Performs theoretical and simulation research on the thermophysical properties of fluids and fluid mixtures, including regions of fluid-fluid and fluid-solid phase separation.
- Develops models and correlations of high accuracy to describe and predict the thermophysical properties of fluids and fluid mixtures.
- Provides comprehensive and evaluated Standard Reference Data and electronic databases for the properties of technically important fluids and fluid mixtures.

Cryogenic Technologies Group (Boulder)

- Develops improved measurement and modeling techniques for characterizing basic cryocooler components and processes.
- Develops prototype state-of-the-art cryocoolers for specific applications.
- Provides measurement standards and services for flow under cryogenic conditions.

Staff Recognition for Fiscal Year 2001

- **Michael J. Kurylo** received two NASA Group Achievement Awards for the successful development of the Earth Science Enterprise Research Strategy 2000-2010 (June 2001) and for the outstanding accomplishments of and contributions to the 1999/2001 SAGE III Ozone Loss and Validation Experiment aircraft and balloon campaign (July 2001).
- **Ray Radebaugh** received the NIST Jacob Rabinow Applied Research Award for advancing the state of the art of cryogenic refrigeration systems for applications in such diverse fields as health, communications, environment, energy, space, defense, chemical analysis, radio astronomy, and microelectronics.
- **Eric Lemmon, Mark McLinden, and Dan Friend** received the NIST Judson C. French for the development of the NIST Pure Fluids Standard Reference Database that dramatically upgrades a key part of the Nation's metrology infrastructure by nearly doubling the number of fluids covered and greatly improving its quality and usability.
- **Dan Friend** received the U.S. Department of Commerce Bronze Medal for his outstanding achievements in advancing the state of the art in the theory for thermophysical properties of industrially important fluids and fluid mixtures.
- **Ray Mountain** was elected a Fellow of the American Physical Society in recognition of his outstanding contributions towards an improved understanding of structural and dynamic properties of simple and complex liquids.
- **Ray Radebaugh and Eric Marquardt** received the 2001 Russell B. Scott Award for the best applications paper "Pulse Tube Oxygen Liquefier" presented at the 1999 CEC/ICMC Conference and published in *Advances in Cryogenic Engineering*.
- **Ray Radebaugh** received the Robert W. Vance Award from the Cryogenic Society of America in recognition of his dedication and long-term commitment of time and energy to the advancement of the field of cryogenics and programs sponsored by this society.

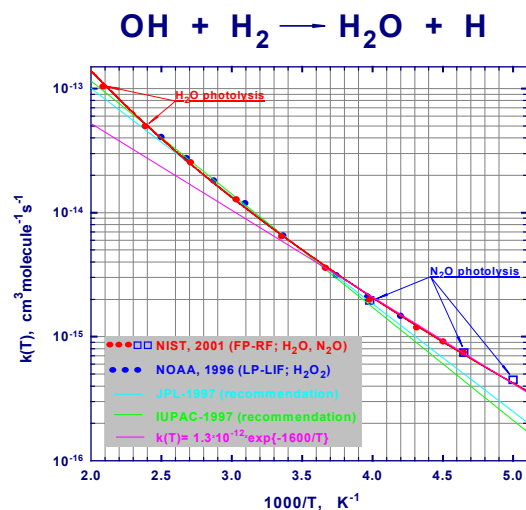
Kinetics of Reactions of the Hydroxyl Radical

CSTL Programs: Chemical and Biochemical Data, Environmental Measurements

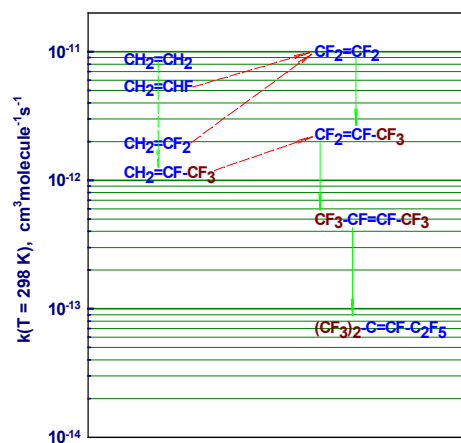
Authors: V.L. Orkin, M.J. Kurylo, and R.E. Huie

Abstract: Rate constants for the reactions of hydroxyl radicals are obtained utilizing the flash photolysis-resonance fluorescence technique over a wide range of experimental conditions. In addition, *ab initio* computational studies are carried out to extend the range of compounds for which reliable information is available. The goal of this activity is to provide a key element of a “screening tool” for the environmental acceptability of new industrial compounds. Indeed, our experimental studies typically have involved the reactions of OH with industrial gases in order to assess their likely environmental impact. Thus, in the past year we investigated the reactions of methyl chloride, n-bromopropane, and a series of perfluorinated alkenes. In addition, we made a very careful study of the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$, extending the lower temperature for which precise and accurate measurements exist down to 200 K. This study is important not only because of environmental concerns. It was also undertaken since it should allow rigorous tests of the computational tools that are being developed, particularly the tunneling correction. This in turn will allow more reliable computations of the reactivity of larger compounds.

Purpose: Reactions of the hydroxyl radical in the gas phase are central to atmospheric chemistry and combustion processes, while those in the liquid phase are key to free radical physiological damage and to many advanced oxidation processes. We are engaged in a combined experimental and computational program to obtain reliable rate constants for selected gas-phase reactions.



Reactivity of Fluorinated Alkenes toward OH



Major Accomplishments: The rate constant for the reaction of OH with H_2 was measured over the temperature range 200 K to 480 K. The data exhibit noticeable curvature at low temperatures and indicate an underestimation of the low temperature rate constant in the current recommendations. The reactions of four perfluorinated alkenes ($\text{CF}_2=\text{CF}_2$, $\text{CF}_3\text{-CF=CF-CF}_3$, $(\text{CF}_3)_2\text{C=CF-C}_2\text{F}_5$, $\text{CF}_2=\text{CF-CF}_3$) with OH were studied between 230 K and 480 K. The Arrhenius plots for these reactions were strongly curved, with the nature of the curvature dependent on the extent of $-\text{CF}_3$ substitution. At room temperature, the substitution of a CF_3

group for a F atom leads to a considerable reduction in the rate constant and, thus, an increase in the expected atmospheric lifetime of the compound.

We have continued our studies of the effect of bromine substitution on reactivity, since compounds containing bromine are ongoing candidates for fire suppression. In the past year, we measured the rate constants for the reactions of OH with n-bromopropane and with 2-bromo-1,1-difluoromethyl ether, over the temperature range 210 K and 230 K to 480 K, respectively.

Impact: These studies have provided the fundamental information required to establish the atmospheric lifetimes for these compounds, and thus estimates of the ozone depletion potential and global warming potential. The study of the reaction of OH with H₂ will provide computational chemists with a key test of approaches to calculating tunneling corrections, which are presently under development.

Future Plans: We are continuing and expanding our computational studies on OH reactivity. We expect to have computations completed on a series of CF₃CXYZ compounds, where X, Y, and Z are F, Cl, and Br, respectively. This work will then be extended to include haloethers. We want to further simplify the computational approach to improve its applicability to larger compounds.

A major experimental goal is to go beyond the simple hydroxyl radical kinetic studies to a more complete study of the atmospheric fate of the compounds. Thus, we want to be able to predict the complete degradation mechanism in the atmosphere following the initial OH attack. This will require the development of new experimental capabilities including, for example, a discharge-flow system coupled to a mass spectrometer.

Kinetics Database on the Web

CSTL Program: Chemical and Biochemical Data

Authors: *T.C. Allison, R.D. Levin, C.-Y. Lin (Contractor), and R.E. Huie*

Abstract: The NIST Chemical Kinetics Database has been updated and made available via the World Wide Web. This new version of the database gives the users powerful searching capabilities, more options for unit conversions, a tabular display of rate constant data, and a plotting interface. The database is linked to the NIST Chemistry WebBook wherever possible. Users now have the ability to access Targeted Evaluations that contain recommended values for kinetic and thermodynamic quantities obtained via extensive literature review. The Targeted Evaluations area also contains a JANAF-type display of thermodynamic data derived from *ab initio* calculations. These data are also available in the NASA polynomial format. All of these features are available through a simple and intuitive web interface, which may be found at <http://kinetics.nist.gov>. In the coming year enhancements to the database will concentrate on the delivery of data in useful formats and on interfacing with other databases and projects. In particular, we will add the ability to import and export data in an XML-based format.

Purpose: The NIST Chemical Kinetics Database is one of the largest collections of chemical kinetics data available and is an extremely valuable resource for researchers in a number of scientific fields. A few years ago a project was initiated to redesign the database so that it could be accessed via the World Wide Web. Since that time we have sought to keep the data in the database current, improve the user interface, and add new features for data searching, retrieval, manipulation, and delivery. We continue to improve the database in response to user comments as well as according to our own development plans.

Major Accomplishments: The NIST Chemical Kinetics Database has been rewritten in a web-accessible format. All of the major features of the Windows-based version have been reproduced. A number of these features have been enhanced such as the searching capability. The user interface of the database has been redesigned to make it more informative, useful, and accessible to other databases or web sites. A Targeted Evaluations section has augmented the database. This section contains comprehensive reviews of the chemical literature for selected chemistries and gives recommended values for thermochemical and kinetic data. Targeted Evaluations also include data derived from *ab initio* computations that may be manipulated through a web-based interface by the user. At present the user has the ability to produce detailed thermodynamic quantities or a JANAF-type table of thermochemical data over a user-selected temperature range. These data are returned to the user in a tabular format as well as in the NASA polynomial format, which may be used directly in kinetic modeling programs such as ChemKin. The NIST Chemical Kinetics Database is linked to the NIST Chemistry WebBook wherever possible. The database web site also contains extensive help and links to relevant internal and external web sites.

At the present time, the NIST Chemical Kinetics Database contains data from more than 12,000 journal articles. It contains more than 38,000 pieces of data on more than 11,700 distinct reactant pairs.

Impact: The NIST Chemical Kinetics Database is the largest collection of rate constant and related data on gas-phase chemical reactions available. Researchers in many different fields across the country and around the world make use of it. It is used in a number of industries and academic institutions in the United States. The database is particularly important to researchers doing kinetic modeling in combustion, atmospheric chemistry, chemical vapor deposition, and other areas.

Future Plans: In the coming year we will launch a major new initiative in quality control. This initiative will include more formal responsibilities for specific quality control issues within staff assignments as well as new software tools. The software tools will allow the entire quality control process to take place electronically. This will, in turn, allow more frequent updates to the database. Also under development are new distributed tools for data entry. These tools are important as we change the way we go about abstracting data from the literature. The data entry tools we are developing will allow people working from any computer to enter data and upload it to NIST. Another major development plan for this year involves the use of the extensible markup language (XML). We will develop XML-based data formats for the NIST Chemical Kinetics Database as well as for other projects. A number of software tools for the entry, manipulation, archival, retrieval, and dissemination of data in these XML-based formats will be developed as well. The database will be extended to allow its data to be shared with other databases or web sites via this XML-based format.

Standards for Calorimetry and Thermodynamics

CSTL Programs: International Measurement Standards, Chemical and Biochemical Data

Authors: *D.R. Kirklin, and D.G. Archer*

Abstract: Thermodynamic and calorimetric measurements have wide usage, ranging from product specification and quality control to research. Many calorimetric or thermodynamic instruments must be calibrated and/or validated for proper operation. Standard Reference Materials and other highly accurate property data for calibration and/or validation of calorimetry and other thermodynamic measurements have been developed. Certification measurements for two new SRMs for calibration of differential scanning calorimeters that operate at subambient to ambient temperatures were made with newly designed and constructed apparatus. Certification of a renewal lot of SRM 217 by combustion calorimetry was also conducted this year. This SRM is used for validation of measurement practices for volatile fuels. A description of our previous high accuracy, enthalpy-of-solution measurements for sodium chloride has now been completed and accepted for publication. These measurements establish this material as a convenient reference material for solution calorimeters. At the request of parties from PTB, IUPAC, and GEFTA, a guide for the practice of conversion of thermodynamic properties from one international temperature scale basis to another was prepared. This guide provides analysis and revision of the thermodynamic properties for two of NIST's calorimetric SRMs; SRM 715, polystyrene, and SRM 781, molybdenum.

Purpose: The objectives of this work are (1) to provide reference materials and reference data of the highest accuracy for calibration and/or validation of calorimetric and thermodynamic procedures and measurements and (2) to provide assistance in the development of consensus standards and the removal of standards-related barriers to trade.

The use of calorimetric and thermodynamic measurements ranges from product specification and quality control of manufacturing to state-of-the-art research. In response to these needs, at least 14 current Standard Reference Materials (SRMs) for calorimetry have been developed. Several non-SRM standards used for calorimetry, densimetry, and isopiestic determination of vapor pressure have also been developed. The development of new standards and participation with voluntary standards organizations continue.

Major Accomplishments: This fiscal year, certification measurements were made for two new SRMs and for renewal of one existing SRM. The new SRMs are the first two of four new SRMs that will serve as a calibration basis for differential scanning calorimetry (DSC) and other thermal analysis methods for temperatures from 100 K to 700 K. The certifications required construction of new calorimetric and sample-handling apparatus. The new SRMs, cyclopentane and gallium, can be used to calibrate DSC over the temperature range of 100 K to 300 K. These two SRMs are particularly important because low-temperature calibration of DSC must be accomplished with organic materials, which are not generally available in sufficient purity to be used in concert with literature values of temperatures and enthalpies of phase changes. There have been discrepancies in the literature for the value of the enthalpy of fusion of gallium, resulting in rather large uncertainties for calibration with this material. The certification measurements for a very pure sample of gallium will eliminate the controversy. A new lot of SRM

217 isooctane, 2,2,4-trimethylpentane was recertified by oxygen combustion measurements, the previous lot having been exhausted. This SRM is used for validation of combustion measurements of volatile fuels.

An article that describes our new enthalpy of solution results for sodium chloride has been written and accepted for publication. These new measurements, more accurate than any that have preceded them, were made with a unique adiabatic enthalpy of solution calorimeter and establish sodium chloride as a convenient standard for testing solution calorimeters. At the request of parties from PTB, GEFTA, and IUPAC, an article was written that describes a method for adjusting thermodynamic properties of materials, particularly calorimetric reference materials, for changes in international temperature-scale basis. This year, a staff member from the PTB of Germany has begun a visit under the terms of the Memorandum of Understanding that was signed between NIST and PTB for observation of our calibration protocols for calorimetric reference materials for differential scanning calorimetry.

Impact: These accomplishments will allow NIST customers to perform accurate calibration of instrumentation and validation of measurement methods. As one example of the previous impact of one of these standards, the previous standard reference equations for the properties of sodium chloride solutions have been cited in research papers more than 120 times, mostly as a measurement standard, and have been used in oil-exploration seismic models.

Future Plans: In FY2002, we expect to finish work on a new adiabatic high-temperature calorimeter, which will be used for certification of SRMs 2235 and 2236. These two SRMs are for calibration of differential scanning calorimeters for temperatures up to 700 K.

Thermodynamic Properties for Environmental Fate and Risk Evaluation: Arsenic and Chromium

CSTL Programs: Chemical and Biochemical Data, Environmental Measurements.

Authors: *D.R. Kirklin, and D.G. Archer*

Abstract: Water simulators are used to model and predict product distributions of species in ground water, in surface water, and in application of remediation technologies. These simulators are written and used by various governmental and private entities. Incorporated within the simulators are thermodynamic databases. The thermodynamic data for many of the species that result from interaction of heavy metals with ground water or surface water components in these databases are often not of sufficient accuracy for the simulators to calculate accurate species distributions. This year we directed our attention to thermodynamic properties of arsenic species and to species important in determining the Cr(VI)-Cr(III) reduction potential. A new table of thermodynamically consistent properties for arsenic species was developed. New measurements were made for substances key in the pathway for determination of the formation properties of aqueous chromium ions, both hexavalent and trivalent. A new equation of state for the potassium sulfate + water system was also prepared. This last system is essential for determination of the properties of the aqueous sulfate ion, a common component in natural waters.

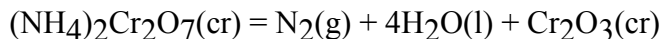
Purpose: The objective of this work is to provide thermodynamic information necessary for prediction of movement of heavy metals through ground waters (aquifers) and surface waters, and for prediction of remediation yields in treatment methodologies.

Natural-water simulators necessarily incorporate thermodynamic information, which often determines the fate of materials in aqueous environments. The models sometimes fail to give observed results, particularly for environmentally sensitive heavy metals. Failures of simulated product distributions often have been traced to faulty thermodynamic information for the products of interaction of these metals with other substances found in natural waters. An inability to predict the level of heavy metals in a lake, aquifer, or remediation methodology interferes with the design of efficient remediation processes.

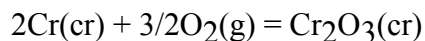
Arsenic is the number one substance on the 1999 CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) List of Priority Hazardous Substances. Chromium also falls high on the CERCLA List. Potential natural attenuation of more toxic Cr(VI) species to less toxic Cr(III) species in aquifers can affect potential remediation requirements. One of the most important parameters affecting calculation of attenuation capacities is the reduction potential of the Cr(VI)-Cr(III) couple. Our previous analysis of the chromium literature indicated several unresolved problems in the thermodynamic information used to calculate this reduction potential.

Major Accomplishments: A new set of thermodynamic properties has been developed for principal mineral and aqueous arsenic species that are involved in ecological or geothermal environments. This new set of thermodynamically consistent properties resolves discrepancies in previous thermodynamic tables for the arsenic oxide minerals and arsenic sulfides. This work resulted from collaboration between the NIST and USGS's Water Resources Division.

This fiscal year we have conducted new measurements that yield thermodynamic properties for substances that lead to the Gibbs energy of formation of the aqueous hexavalent chromium ion, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$. The first of these measurements was redetermination of the enthalpy of decomposition of ammonium dichromate:



Our analysis of the reaction products does not support the assumption that the reactant was completely consumed; the reactant is not completely consumed. Therefore, our new enthalpy of reaction is significantly different than the earlier value. We have initiated a series of combustion measurements on chromium:



Our preliminary results do not support the tabulated thermodynamic properties for $\text{Cr}_2\text{O}_3(\text{cr})$, which lead subsequently to the thermodynamic properties for the aqueous trivalent chromium ion. Therefore, there is doubt as to the true reduction potential for the Cr(VI)-Cr(III) couple.

A new equation of state for the potassium sulfate + water system was prepared. This equation of state is a significant improvement over earlier equations that have been used for predicting solubilities in geothermal applications and as a standard for a type of electrode. An accurate equation of state for this system is required also for the eventual determination of accurate properties of aqueous sulfate ion, a component in many natural waters and industrial processes.

Impact: The importance of research on heavy metal distribution and remediation was expressed in the recent background paper on future opportunities for NIST.¹ The new chromium measurements will lead to more accurate values for the Cr(VI)-Cr(III) reduction couple. These new properties and those for arsenic will be incorporated into simulators used by numerous private and government entities.

Future Plans: New determinations of thermodynamic properties of other key heavy metal species will be undertaken to improve the predictive ability of simulation.

¹ "Trends in Science and Technology. A Background Paper for the National Research Council Committee on Future Environments for the National Institute of Standards and Technology." P. Young, 2001.

Chemistry and Properties of Trace Components of Fuel Gas

CSTL Program: Physical Property Data

Authors: *T.J. Bruno, W.C. Andersen, A.F. Lagalante, and G.M. Bachmeyer (Contractor); A. Abdulagatov (Dagestan Scientific Center of Russian Academy of Sciences), and K.I. Henning (Institute Louis Pasteur, France)*

Abstract: The United States consumes approximately 22 trillion cubic feet of fuel gas each year, with fuel gas being defined broadly as natural gas and liquefied petroleum gas. Natural gas consists primarily of methane, but between 300 and 400 additional compounds may be present at varying levels. Most of these additional materials are naturally occurring, consisting of heavier hydrocarbons, sulfur compounds, water, carbon dioxide, etc., and some are added intentionally during processing. Liquefied petroleum gas (LPG) consists primarily of propane, but again, many other compounds are present in the industrial product. Most fuel gas is used industrially, and for electric power generation, with 20 percent used in residential applications. The efficient and safe design of plant equipment operated with fuel gases critically depends upon knowledge of the properties and chemistry of individual components of natural gas and LPG. Moreover, it has become very clear that the components present at minor levels (or even at trace quantities) can have a significant impact on the overall properties of the fuel gas mixture.

Purpose: To provide the natural gas industry with chemical characterization and properties that are critically needed for the efficient operation of fuel gas processing, transmission and distribution. This is required for custody transfer, calorific value, quality control, safety and environmental compliance.

Major Accomplishments: Our most recent work has included (1) development of chromatographic databases for trace compound identification, (2) measurement of odorant adsorption on soil, and (3) measurement of the hydrolysis reaction of carbonyl sulfide (COS) in propane. The chromatographic databases are tools to allow identification of trace components on the basis of retention indices. These databases are used in ASTM methods requiring the determination of gas composition. The final versions of the databases were released this year, with one edition for hydrocarbons and one for odorant compounds. The problem of odorant fading led to our work on the adsorption of sulfur odorants in natural gas. We measured the enthalpy of adsorption, ΔH_{ads} , of odorants on soil surrogates (clay and an organo-clay). These measurements were done with a chromatographic approach developed at NIST. A significant result is the observation of a very high ΔH_{ads} for tetrahydrothiophene and a relatively low ΔH_{ads} for t-butyl mercaptan. In LPG, we have measured the kinetics of COS hydrolysis. We have discovered that the hydrolysis only occurs in a separate aqueous phase, not in water dissolved in LPG. Moreover, we have determined that the reaction rate is very slow at typical temperatures. Moreover, we have developed a molecular recognition separation method to remove COS from LPG.

Impact: Our chromatographic databases are used by transmission/distribution companies in natural gas analyses. Our relatively recent work on the hydrolysis of COS will impact the processing action levels for trace components in LPG. The (very common) presence of clay in a

pipeline, or the leak of gas through a clay soil can have devastating consequences. The discovery of the disparity in adsorption of the various natural gas odorants will allow avoidance of unfavorable odorants, and thereby improve safety.

Future Plans: Our work on odorant adsorption will be extended to hydrated organoclays. We are also developing an improved method for copper strip corrosion testing for all fuel gas products.

Publications:

Bruno, T.J. and Rybowiak, M.C., *“A Vapor Entraining Magnetic Mixer for Equilibrium and Reaction Applications,”* Fluid Phase Equil. 178, 271 (2001).

Bruno, T.J. and Lagalante, A.F., *“Method for Removal of Carbonyl Sulfide from LPG Streams,”* United States Patent (to issue December 2001).

Bruno, T.J., Andersen, W.C., and Henning, K.I., *“Hydrolysis of Carbonyl Sulfide: A Potential Source of Downstream Sour Gas,”* Proc. GTI Conf. Gas Qual. and Odorization, Chicago, Illinois (2001).

Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes

CSTL Programs: Physical Property Data, Environmental Measurements

Authors: *T.J. Bruno, K.E. Miller, and H.J.M. Hanley; and F. Tsvetkov (Daren Laboratories, Nez Ziona, Israel)*

Abstract: Clays are used in a broad array of applications including pollution prevention and remediation, enhanced oil recovery, the treatment of petroleum liquids, the manufacture of cosmetics and pharmaceuticals, and the synthesis of polymer nanocomposite materials. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a critical issue for future developments in all of these applications. In order to understand the physical chemistry (both thermodynamics and kinetics) of the clay-solute interaction, we have advanced the application of physicochemical gas chromatography by devising stable clay- and organoclay-coated capillary columns. The capillary column approach we have developed is more efficient, requires lower temperatures, and produces enthalpy of adsorption (H_{ads}) with a much lower uncertainty than the conventional techniques.

Purpose: Our goal is to exploit the unique characteristics of clay platelets in the production of organic-inorganic composite materials with revolutionary material properties and in the development of novel chemical separation and material characterization techniques.

Major Accomplishments: We have measured the enthalpy of adsorption (H_{ads}) for a family of hydrocarbons on Laponite and Laponite complexed with CTAB. The CTAB-coated Laponite is especially significant for environmental remediation because it represents a surrogate soil system that can be used to better understand the interaction of pollutants on soils. Our results indicate that washing (or weathering) has a significant effect on the strength of the pollutant-clay interaction. In addition to the environmental work, we measured ΔH_{ads} of natural gas odorant compounds on soil surrogates (a clay and an organo-clay). This was motivated by the observation of odorant fading in fuel gas, a suspected cause of which is adsorption on soils. A significant result is the observation of a very high ΔH_{ads} for tetrahydrothiophene, and a relatively low ΔH_{ads} for tert-butyl mercaptan. We have recently expanded our physicochemical chromatographic efforts to include liquid systems, using the instrumentation of HPLC. This work has centered on the production of stable clay packings for HPLC columns. We have developed spray drying and heat-treating techniques that produce stable spherical clay particles 2 to 5 μm in diameter. These stable packings enable the determination of enthalpy of interactions of organic solutes with clay and organo-clay surfaces in aqueous phase solutions. Initial measurements on pure Laponite surfaces indicate that the interaction between aromatic hydrocarbons and the hydrated clay surface is minimal. Enthalpies of CTAB-coated Laponite particles, however, indicate that the surfaces of the organo-clay significantly alter the adsorption characteristics of the media, and that these organo-clay surfaces are strongly hydrophobic.

Impact: An example of an immediate impact of this work is the disparity in adsorption of the various natural gas odorants. The (very common) presence of clay in a pipeline or the leak of a pipe up through a clay soil can have devastating consequences. Our results will allow avoidance

of unfavorable odorants, and thereby improve safety. As an example of a long term impact, our measurements on liquid systems will allow prediction of pollutant entry into ground waters.

Future Plans: Presently, the clay particles are being examined by x-ray diffraction, scanning-electron microscopy, and thermo-gravimetric analyses to quantify the degree to which the clay characteristics have been modified. Future work in this area includes development of particles with a higher porosity, and thus greater surface area. In addition, near-term measurements are planned for aqueous phase ΔH measurements of environmentally important classes of compounds including polar pesticides and nitro-aromatics, including explosive components and their degradation products.

Properties and Processes for Cryogenic Refrigeration

CSTL Program: Process Metrology

Authors: *R. Radebaugh, P. Bradley, and M. Lewis; R. Gates, L. Reynolds, and J. Le (Univ. of Colorado); J. Gary, and A. O'Gallagher (891)*

Abstract: The objectives of this research are (1) to use measurement and modeling techniques for evaluating and improving performance of cryocoolers and their components, such as heat exchangers and pulse tubes, (2) to develop new and improved refrigeration and heat transfer processes for the temperature range below about 230 K, and (3) to provide a database on material properties at cryogenic temperatures. Our regenerator modeling has been expanded to include the effect of superimposed dc flow and heat intercepts along the length, as well as improved convergence for modeling 4 K cryocoolers. These improved models were used extensively this past year in the preparation of a paper on regenerator optimization for operation at 4K as well as in modeling for industrial customers to assist them in developing new cryocoolers. A prototype pulse tube neon liquefier to provide 500 W at 30 K was modeled, optimized, and in development under a CRADA to learn more about the scale-up of this technology into large industrial applications. A web site was developed for our database on properties of solid materials at cryogenic temperatures. About 50 materials are now posted, and properties include thermal conductivity, specific heat, and thermal expansion. Mechanical properties are currently being added.

Purpose: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics, magnets, and power systems, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas, and many other existing and potential applications. The use of these technologies has been hampered because of problems with existing cryocoolers. These problems include short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas. Proper measurements need to be identified that will characterize losses within these cryocoolers and models need to be developed to optimize the design of such systems. Material properties at cryogenic temperatures are needed by industry for the design of cryogenic equipment, but the data are difficult to find and often in out-of-print reports.

Major Accomplishments: Two book chapters reviewing the status of cryocoolers for use with superconductors were completed and are now undergoing review. An improved numerical model was developed for faster operation and better convergence in the modeling of regenerators operating at 4 K. This model along with our earlier model REGEN3.2 were used in the preparation of a paper on methods for optimizing regenerators in this low temperature range and how their efficiency can be improved. A large (500 W at 30 K) prototype pulse tube neon liquefier was modeled, optimized, and nearly completed under a CRADA with an industrial sponsor. Extensive instrumentation has been added to understand the physics and the source of losses in the scale-up of pulse tube refrigerators. Over 15 new materials have been added to our cryogenic materials database and a new web site developed to deal with the larger data set.

Impact: Our accomplishments this year have provided industry with new tools to improve the performance of cryocoolers, particularly those operating at temperatures below about 20 K. The review chapters on cryocoolers will aid the superconductor industry in the development of superconducting systems that can be marketed to a larger customer base. Our materials properties database is now getting more attention and is useful to all industries dealing with cryogenic temperatures.

Future Plans: Activity in this area is continually expanding as more industrial customers are requiring our models, data, and technical expertise in the development of cryocoolers for an ever-increasing range of applications. To improve efficiency of these coolers, we are planning on the development of a test apparatus to measure nearly all types of losses in cryocoolers and to measure how they are influenced by various parameters. The results will be used in the development of improved models.

Microscale Heat Transfer

CSTL Program: Process Metrology

Authors: *R. Radebaugh, P. Bradley, and M. Lewis; and J. Pfotenhauer (Univ. of Wisconsin)*

Abstract: The objectives of this research are (1) to perform measurements to help develop models to predict heat transfer coefficients and friction factors in single-phase and two-phase flow within geometries that have characteristic lengths comparable with that of the heat transport mechanism, such as mean free path or bubble dimensions, and (2) to develop models and measurement procedures for characterizing heat and mass transfer in fluid systems with short time scales, such as with transient or rapidly oscillating systems. Microscale fluid systems do not behave as larger scale bulk fluid systems, yet microscale devices must be designed to allow precisely controlled fluid and chemical processes. Such designs require data and models applicable to the range of conditions that occur in microscale devices. During FY2001 we have developed a measurement apparatus to characterize microscale heat exchangers from temperatures of about 20 K to 300 K. A test parallel plate microscale heat exchanger utilizing photoetching and diffusion bonding techniques was developed and is ready for testing.

Purpose: Microscale fluid systems do not behave as larger scale bulk fluid systems, yet microscale devices must be designed to allow precisely controlled fluid and chemical processes. Such designs require data and models applicable to the range of conditions that occur in microscale devices. Because such data and models are lacking, current modeling is based on bulk properties and processes that may not be representative of their behavior in microscale environments. The electronics industry has experienced spectacular advances in electronic devices and systems by utilizing the benefits afforded by microfabrication. Similar advances in the chemical industry may occur with widespread use of microreactors and microfluidic systems. The unique features of microdevices are the very large surface-to-volume ratios that are achieved and the very short time scales involved with processes. Many microscale devices utilize some form of heat transfer. Heat transfer coefficients and friction factors in microscale devices are different than in macroscale devices, and models for predicting heat transfer and pressure drop in microscale devices are almost nonexistent. Models for heat transfer and fluid flow in macroscale devices are no longer valid when the characteristic fluid dimension, such as bubble size in boiling heat transfer or the boundary layer in single phase heat and mass transfer, is comparable to or larger than the channel dimension. The fluid properties in these thin boundary layers may be different from the bulk fluid properties due to enhance influence from surface and electrostatic effects. The second area of microscale heat and mass transfer involves short time scales as experienced in transient or oscillating thermodynamic systems. Models and empirical correlations for heat transfer and pressure drop obtained for steady state flows in large systems are no longer valid for very short time scales.

Major Accomplishments: During FY01 microscale heat exchangers with parallel plate geometry and with flow channels designed to reduce flow maldistribution were developed for use in miniaturizing recuperative cryocoolers. The development included the use of NIST computer models to optimize the geometry, photoetching of flow channels in each plate, and the diffusion bonding of the stainless steel plates. Flow channels and plate thicknesses were in the range of 100 to 150 μm . An apparatus to measure the friction factors and number of heat

transfer units in these microscale heat exchangers between about 20 and 300 K was also developed. An apparatus to measure heat and mass transfer characteristics under oscillating flow conditions up to 60 Hz was designed conceptually and two major equipment items for the system were purchased. Detailed designs of the system components and measurement procedures are now underway. An analytical model for oscillating bubbles in metastable fluids was developed and presented at a division seminar. An experimental apparatus utilizing glass slides and laser heating to study explosive boiling of superheated liquids in microscale geometries is under development.

Impact: The microscale heat exchangers currently being developed in this program should lead to considerable size and weight reductions in Joule-Thomson and Brayton cycle cryocoolers. The heat exchanger is presently the largest component in most Brayton cryocoolers, and it is the largest low temperature component in Joule-Thomson cryocoolers. The use of microscale devices would significantly reduce the size and weight of cryocoolers used in space for military or commercial applications.

Future Plans: Measurements of friction factors and heat transfer coefficients for the parallel-plate microscale heat exchangers will be carried out at temperature from about 40 K to 300 K. The results will be compared with our models and with results from larger systems. We expect to begin measurements of friction factors and heat transfer coefficients in regenerators undergoing oscillating flow at frequencies between 30 and 60 Hz. These results will be compared with steady state correlations.

Computational Chemistry Comparison and Benchmark Database

CSTL Program: Chemical and Biochemical Data

Author: *R.D. Johnson III*

Abstract: The Computational Chemistry Comparison and Benchmark Database (CCCBDB) is designed to answer the question "How good is that quantum chemistry calculation for a given property?" The database contains the results from over 50,000 calculations on 615 molecules of industrial interest for which good thermal and spectral experimental data are available. Comparative results are displayed graphically for easy interpretation. Tutorials are implemented to guide the user through the process of selecting the optimum computational method to obtain the property of interest, and to understand the inherent magnitudes and sources of error. About 4,000 web pages are served every month.

Purpose: The CCCBDB provides a benchmark set of molecules for the development and evaluation of new theoretical methods. It also provides users with a readily accessible means of comparing existing computational chemistry methods with experiment and analyzing the magnitude of error in computed thermochemical properties associated with time-saving approximations. The initial focus of the database was exclusively thermochemistry and structure, but has recently been expanded to include other properties of interest to the chemical industry, such as transition state structures and energies for kinetics, dipole moments, and ionization energies. The CCCBDB contains a set of 615 benchmark molecules with reliable thermochemical and spectral data for which both the experimental values and uncertainties have been evaluated. We are generating data from *ab initio* calculations for comparison with each other and with experiment.

Major Accomplishments: The website has been running since November 1999. The URL is: <http://srdata.nist.gov/cccbdb>. The data has continuously expanded, and as of September 2001 there are over 50,000 computational results available (up from 30,000 last year). Experimental data has included enthalpies, entropies, integrated heat capacities, vibrational frequencies, rotational constants, bond lengths and angles, and electronic energy levels. New data in the latest release include heat capacities, bond descriptions for isodesmic reaction predictions, electric dipole moments, ionization energies, and barriers to internal rotation (which are needed for the accurate prediction of entropies). Computed data include all of the above as well as atomic charges, HOMO-LUMO gaps, and diagnostics for the calculations. The calculations cover 25 different theoretical methods and seventeen basis sets. To make the database more useful and educational to non-expert users of computational chemistry, a series of tutorials and easy-to-understand visualizations of the comparative results have been implemented. The most recent tutorials are: obtaining enthalpy of formation from the results of *ab initio* calculations, converting an enthalpy from 0 K to 298.15 K, scaling of vibrational frequencies, and vertical versus adiabatic ionization energies.

Impact: The website serves about 4000 pages a month. Not all industrial companies have a full time computational chemistry expert on staff, yet many are using the programs available to obtain properties of interest. Hence, the CCCBDB website is designed to enable the non-expert

academic or industrial user to choose the optimum method available to calculate properties of interest, and to understand the inherent magnitude and sources of error in the calculation.

Future Plans: Running the *ab initio* quantum mechanical calculations is an ongoing activity, as is the development of tools for viewing and accessing the data over the web. Extensions of the current data set to include the most recently developed methods and basis sets are continuing. Data are being collected from users on what species should be added to the CCCBDB, both passively (whenever someone request information on a species that is not present in the CCCBDB that species is recorded) and actively (through a form in which users can request the addition of molecules, methods and properties). New directions important to the chemical industry are NMR shifts, transition states, UV/VIS spectra, ionization energies, molecular mechanics methods, and group additivity methods. The data are also being mined to reveal problems with existing theories, such as known stable molecules that are calculated to be unbound at certain levels of theory, and molecules whose geometry changes significantly depending upon the method used. The molecules and methods thus identified as being problematic are added to the “Computational Chemistry Sicklist” <http://srdata.nist.gov/sicklist> and used to indicate where additional research needs to be done.

Theoretical Studies of Electrical Conductance in Molecular Wires

CSTL Program: Nanotechnology

Author: C.A. Gonzalez

Abstract: Recently, there has been increased interest in molecular electronics due to the prospect of designing efficient electronic nano-scale components that could exhibit functionalities not achievable with silicon devices (e.g., optical emitters). Despite the significant progress made in the development of techniques to fabricate and characterize molecular conductors, as well as in the theoretical understanding of the mechanisms involved in electronic conduction through molecules bounded to metallic surfaces, the fact remains that molecular electronics is currently more of an art than a science characterized by a significant lack of reproducibility. Clearly, there is a marked need for the development of robust theoretical and experimental tools that could be used on a routine basis in the design of novel materials leading to the development of reliable electronic devices based on molecular electronics. In this work, reliable and efficient theoretical methodologies that lead to the understanding of the fundamental mechanisms governing electrical conductance in materials at the molecular level are being developed.

Purpose: The main idea of this project is to study the electronic transport of molecular wire circuits using a time-independent Landauer scattering formalism based on a first-order expansion of the system Green's function. All calculations include an *ab initio* description of the molecular electronic structure. The molecular bridge is bound to the metallic electrodes by means of thiolate groups at the head and tail of the bridge. Decay length constants are computed and compared with available experimental data. In addition, the effects of electrostatic interactions at the molecule-electrode junction on the current-voltage curve are also studied. It is hoped that the theoretical models developed and validated in this work will provide a set of important tools that will complement the experimental studies conducted by researchers in the nascent molecular electronics industry as well as in research centers available in national labs and universities.

Major Accomplishments: In the initial phase of the project, conductance calculations were carried out on the prototype system $\text{H-S-(CH=CH)}_n\text{-S-H}$ (with $n = 3, 4, 5, 7$), α, α' -xylyl-dithiol and benzene-1,4-dithiol. The decay length constants computed by this simple approach are in excellent agreement with recent experimental measurements. In the case of the di-thiols, it was found that the conductance depends dramatically on the relative position of the Fermi level, E_F , of the metal with respect to the molecular orbital energy levels. In addition, it was found that the injecting energy of the electron onto the molecule lies close to the highest occupied molecular orbital, HOMO, rather than in the middle of the HOMO-LUMO gap. Once again, the results are in excellent agreement with available experimental data.

Impact: Although this study is in its preliminary stage, important information regarding the reliability of the Landauer conductance model has been assessed, and recommendations made for conditions under which it should be applied. The results have been reported in the open literature. In addition, contacts with research groups in places such as Hewlett-Packard, the Naval Research Lab, and Northwestern University have provided positive feedback regarding the importance and scope of this study.

Future Plans: Further work focused on the development of formalisms that properly describe the electrostatics at the molecule-metal junction is underway. These methods will be applied in the calculation of current-voltage plots for a large variety of molecules and metals.

Software for Predicting Chemical Reactivity

CSTL Program: Chemical and Biochemical Data

Author: *K.K. Irikura*

Abstract: New software has been written for predicting and discovering chemical reactions. It employs the “isopotential searching” (IPS) method developed recently at NIST. IPS is a computational procedure in which the atoms of a molecule are moved semi-randomly. The feasibility of the atomic motion is computed quantum mechanically, and the atoms are moved again. The process is repeated until a reaction is discovered. Only those motions are tested that are of approximately equal energy, that is, all tested atomic configurations lie on an isopotential contour. This restriction leads to better efficiency than in conventional simulations. The purpose of the new software is to transfer the IPS technology to researchers outside NIST for use in diverse applications such as reaction design, catalyst screening, mass spectrometry, and reactive hazards evaluation.

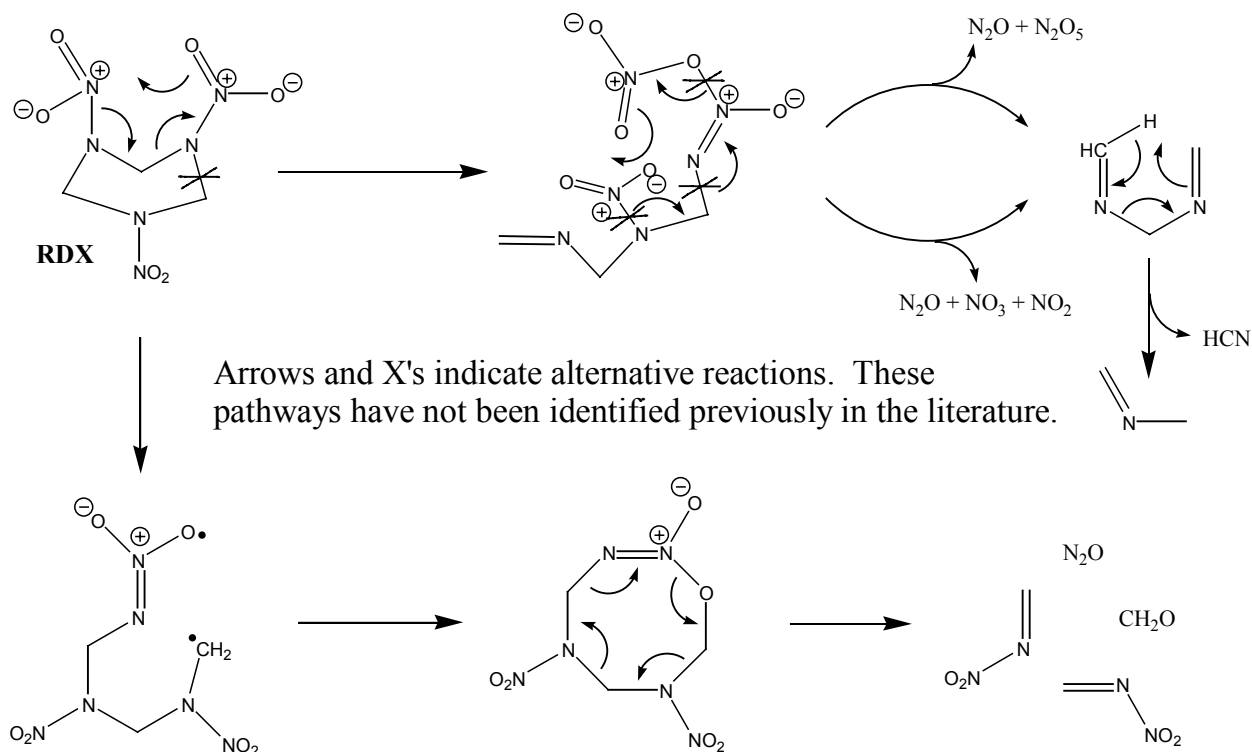
Objective: The objective of this work is to build portable software for predicting the products and mechanisms of reactions of arbitrary molecules.

Purpose: Predicting how molecules will react is one of the most important tasks required of chemists. It is important for many reasons, such as avoiding unwanted side-reactions, designing molecules with desired properties, and controlling thermal or oxidative decomposition. Traditionally, predictions are obtained entirely through a chemist’s intuition. Although this procedure is nearly instantaneous, it is error-prone and limited by the chemist’s knowledge and skill. Subsequent chemical R&D, which is typically expensive, depends upon the accuracy of the intuitive predictions. When intuition falls short, the R&D fails and the entire process must be repeated, resulting in costly losses in productivity. Surprisingly, there is no computer software available for supplementing human chemical intuition.

We recently developed a new method, called “isopotential searching,” that harnesses quantum chemistry to predict chemical reactivity, thus supplementing “chemical intuition.” The successful demonstration of the concept was described in a journal publication [Irikura and Johnson, *J. Phys. Chem. A* 104, 2191 (2000)]. In 2001 the emphasis has been on software development. The program has been completely rewritten for portability and ease of use, with the goal of facilitating the transfer of this technology to researchers in industry and academia.

Major Accomplishments: Instead of a collection of scripts in the *csh* and *awk* languages, we now have a single script in *Perl*, which was chosen for its compatibility with all common operating systems: Windows, UNIX, and Macintosh. The script drives the GAMESS-US quantum chemistry package, which is among the most popular such packages and is freely available to all users. Thus, this choice results in the lowest barrier to widespread use of the NIST techniques. In addition to the new program for isopotential searching, a supplementary code has been developed to aid in the analysis of the results. All results are displayed visually as animations. The new software is now in alpha testing at selected industrial and academic sites.

Impact: Predicting chemical reactions is a core part of chemistry; many areas of impact are anticipated as the technology evolves. Applications in mass spectrometry and combustion chemistry are already in progress. For example, we have already identified some new decomposition mechanisms for the military explosive known as RDX (see figure), which predict that NO_3 and/or N_2O_5 are reaction products. This suggests new strategies for detecting concealed quantities of the compound.



Future Plans: Beta and general releases are planned for FY2002. Wide distribution is a long-term goal. We are also pursuing applications in areas where we expect high impact.

International Cooperation on the Properties of Water and Aqueous Mixtures

CSTL Programs: Physical Property Data, International Measurement Standards

Authors: *D.G. Friend, A.H. Harvey, J.W. Magee, E.W. Lemmon, and J.M.H. Levelt Sengers; and I.M. Abdulagatov (Dagestan Scientific Center of Russian Academy of Sciences)*

Abstract: NIST has been active in work toward international standards for water and steam properties for 80 years. NIST personnel continue to be active in the International Association for the Properties of Water and Steam (IAPWS). IAPWS sets standards for properties of water and key aqueous mixtures, and supports research in aqueous physical chemistry. These standards are widely used in industries such as the electric power industry, where they enable international trade in power generation equipment. Each year, IAPWS holds its annual meeting (consisting of meetings of the Executive Committee representing the member nations of IAPWS and also meetings of the four IAPWS Working Groups) in one of the member nations. In September 2001, the IAPWS annual meeting was held at NIST headquarters in Gaithersburg, Maryland. NIST research toward the goals of IAPWS includes a joint IAPWS project with scientists at the Dagestan branch of the Russian Academy of Sciences for calorimetric measurement of properties of water/methanol mixtures, and a project to produce an updated correlation for the vapor pressure of heavy water (D₂O).

Purpose: International standards for water properties are important, both for scientific studies involving this important substance and so that industry (especially the steam power industry) can have a “level playing field” for design and contracting. These standards are developed and promulgated through the International Association for the Properties of Water and Steam. U.S. representation to IAPWS is through the Properties of Steam Subcommittee of the ASME Research and Technology Committee on Water and Steam in Thermal Systems, which serves as the U.S. National Committee to IAPWS. NIST participation in IAPWS activities serves to ensure that U.S. scientists and engineers have access to important international standards for properties of water and aqueous systems, and that they have a voice in developing those standards.

Major Accomplishments: The U.S. National Committee to IAPWS hosted the 2001 annual meeting, in part to commemorate the Centennial of NBS/NIST. The main local organizing work was done by J.M.H. Levelt Sengers, who is the U.S. National Delegate to IAPWS. She was assisted by Allan Harvey, who in mid-year became the Chair of the U.S. National Committee. The meeting was held in Gaithersburg on September 9-14, and was attended by approximately 60 scientists and engineers from 13 countries. While the events of September 11 caused reshuffling of the schedule (and forced cancellation of a Symposium on *Electric Power of the Future* that had been planned for Sept. 12), the necessary business of the meeting was still accomplished.

IAPWS supported a collaborative project between NIST and the Dagestan branch of the Russian Academy of Sciences. Under this project, isochoric heat capacity measurements of binary mixtures of water and methanol were completed using the twin-bomb adiabatic calorimeter at NIST Boulder, and additional scientific visits were arranged to assist in the development of standard protocols for high-temperature, aqueous calorimetry.

In addition, we thoroughly reviewed the data for the vapor pressure of heavy water (D_2O). There had been several sets of data taken since the last review; the correlation developed at that time does not pass through the coordinates of the critical point as accepted by IAPWS, nor is it on the current ITS-90 temperature scale. A new reference correlation for the vapor pressure of D_2O was produced, covering the range from the triple point to the critical point and representing the data within their scatter.

Impact: NIST's involvement in IAPWS improves international standards for water properties and helps U.S. companies and research institutions stay up to date with the latest and most accurate standards.

Future Plans: We will continue to be a significant part of the U.S. representation to IAPWS, and to pursue research on properties of water and aqueous systems. Work in the near future will include participation in an international effort (joint between IAPWS and IUPAC) to produce standard representations for the viscosity and thermal conductivity of water, a thorough review and correlation of data for the Henry's constants of common gases dissolved in high-temperature water, and work on standards for the properties of simulated models of water.

Measurements, Modeling and Data for Pressure-Driven Membrane Separations

CSTL Program: Physical Property Data

Authors: *C. Muzny, K. Benko, and J. Scott; Y. Yoon and S. Wright (University of Colorado); M. Chapman-Wilbert, and K..Price (U.S. Bureau of Reclamation); and J. Ranville (Colorado School of Mines)*

Abstract: Analysis techniques for the standardization of membrane performance testing in pressure-driven separations are under development. These techniques include methods for the characterization of both the membrane and the complex mixture to which the membranes are subjected for separations testing. The membrane is characterized by a novel liquid-liquid porosimetry apparatus for the measurement of pore-size distributions, while the standard fouling mixtures are characterized by field flow fractionation. By producing a standard fouling mixture that includes particulates and a range of large organic species, we are able to determine membrane performance under a variety of realistic conditions. These standard test solutions and procedures will provide industry with a uniform method for pressure-driven membrane separation performance testing. A modeling effort is also under way to help elucidate fouling mechanisms in ultrafiltration and reverse osmosis membranes.

Purpose: The purpose of this project is to develop standard methods for the determination of membrane performance in pressure-driven separations. The ultimate goal is to provide a standard test mixture for testing membrane fouling along with standard procedures for evaluating membrane performance.

Major Accomplishments: As part of this development, it is necessary to have standard techniques for the evaluation of both the membrane and the test solution. The membrane must be evaluated for chemical, physical, and structural characteristics important in the development of rational design criteria for separations. During the last year membrane characterization has focused on the development of a unique, liquid-liquid porosimetry apparatus for the measurement of membrane pore-size distributions in ultrafiltration membranes. Because of the possibility of using this technique with relatively small pressure drops, it has previously been applied mainly to the measurement of pore-size distributions in structurally weak membranes. However, by a careful choice of displacing fluids together with a differential pressure measurement system that is capable of measuring pressure drops from 69 kPa to 2.8 MPa (0.01 to 400 psia), we have been able to extend this technique to the measurement of pore-size distributions in ultrafiltration membranes. The characterization of a standard fouling solution in the last year has focused on the development of field flow fractionation test procedures and analysis tools for the characterization of all aspects of the fluid, from its smallest molecular and particulate contaminants to its largest organic fouling components. This work has centered on the measurement of standard fouling components individually as a function of concentration and chemical condition. By tuning the field flow fractionation technique, it is possible to separate all of these components. Current work is focused on the characterization of multicomponent systems equivalent to those proposed for standard fouling tests. This technique is intended to provide a method for testing the quality and repeatability of the production of standard fouling solutions.

Impact: Improved processes for obtaining specialty chemicals, pharmaceuticals, and advanced monomers using environmentally benign processes, and more economic ways to recover, reuse, and supply water are examples of important industrial and municipal uses of membranes. All of these areas will benefit from the development of systematic approaches for matching appropriate membranes to complex mixtures, and from the prediction of the relevant filtration figures of merit, species partitioning into the membrane, solvent permeability, and permeability decline over time.

Future Plans: Both the membrane characterization and fouling solution characterization have further work to be done in order to produce reliable measurements. The liquid-liquid porosimetry apparatus has been tested under ideal conditions and will have further evaluation for other membrane/test solvents combinations. This measurement also requires an accurate knowledge of liquid-liquid interfacial energies, and to this end, an apparatus for this measurement will be assembled and tested. A functional, robust pore-size distribution measurement technique for the evaluation of ultrafiltration membranes is the goal of this work during the coming year. The characterization of the standard fouling solutions will also proceed with measurements on standard, multicomponent mixtures under a variety of chemical conditions. The goal will be to provide field flow fractionation testing conditions for the separation of all of these elements. A standard fouling solution along with data characterizing it will then be produced.

Liquid, Vapor, and Gas Transport Properties in Membranes and Films

CSTL Program: Physical Property Data

Authors: *C. Muzny, R. Larsen, and J. Scott; B. Bauer (854); and R. Hedden (854)*

Abstract: Measurements of liquid, vapor, and gas diffusion and sorption in thin layer films are critical for development of techniques to predict membrane transport properties. These measurements provide a means to compile the effects of both chemical and structural subgroups in the material, and ultimately, to delineate rational design criteria for mass separating agents such as membranes and polymeric adsorbents. Measurements of solvent solubility and diffusivity are being made on a variety of thin polymeric films including polypropylene, cellulose acetate, and polysulfone using an FTIR-attenuated total reflectance (ATR) apparatus. In addition, a second, high-throughput apparatus for the measurement of the diffusivity and solubility of a variety of test components in a wide variety of membranes is under development. This technique employs an array of sixteen test cells that are individually temperature controlled and that can be loaded with differing solvents, test solutions and membranes under analysis. A critical component of this method is to have easily detectable, standard test compounds that probe different physical and chemical characteristics of the membranes. Because fluorescence has been selected as the detection technique, this means appropriate fluorophores must be developed. Candidate fluorophores include cadmium sulfide nanocrystals in star polymers, fluorescently tagged star polymers, fluorescently tagged dendrimers of varying numbers of generations, and the family of polyaromatic, nuclear hydrocarbons. These diffusivity and solubility data will be made available via an online database and ultimately will be used in the development of quantitative structure property relations for the prediction of the transport properties of other chemical species.

Purpose: This work is intended to provide critical data for the characterization of membranes and films according to their species-specific transport properties. This data will then be available for use in the rational design of separations processes.

Major Accomplishments: Significant progress has been made in both the application of the previously developed ATR-FTIR method and in the development of a new apparatus for high throughput transport properties measurement. Water diffusion through a variety of commercial polypropylene (PP) membranes was the focus of the ATR-FTIR measurements. In this work a “breakthrough phenomenon” was previously observed and the purpose of these measurements was to elucidate this effect. Thus, PP films of varying thickness with a variety of surface treatments were used for measurements of water diffusivity. The result was that a uniform surface resistance to diffusion was found to be independent of film thickness and nearly independent of surface treatment. However, the bulk diffusivity varied widely as a function of film thickness. This was attributed to a variation in internal structure as a function of thickness due to differing film processing conditions.

Development of a new high throughput apparatus for transport properties measurements has proceeded along several different lines. A control system capable of simultaneously controlling the temperature and fluid flow on both sides of the transport cells for eight individual cells was built and tested. Prototype transport cells have been manufactured and tested. Fast, highly

sensitive in-line fluorescence detection systems have been tested. These systems are based on fiber optic coupling of both excitation and emission light to the individual test cells with the addition of a fiber optic multiplexer to switch the cells into the fluorescence detector. Unique, fluorescent probe molecules have also been manufactured. A cadmium sulfide nanocrystal in a G4 PAMAM dendrimer was evaluated. Its fluorescence properties were determined to be inadequate for this experiment. Subsequently polyethylene glycol star polymers were produced and then fluorescently tagged. Evaluation of these polymers indicates they are excellent candidates for this experiment.

Impact: Although polymeric and inorganic materials are used in membrane and adsorptive separation processes, a significant barrier to the optimum use of existing materials and development of new materials is the lack of predictive capabilities for the transport properties of mixtures in any selected material. This data production effort will facilitate the development of the quantitative structure property relationships necessary for the development of these predictive methods. The availability of both the data and predictive methods will impact all industries that currently use membrane-based separations including the water purification industry, the pharmaceuticals industry, and the chemical industry.

Future Plans: Measurements on a variety of films in the ATR-FTIR apparatus will continue with the results being added to our membrane properties database. Development of the high throughput membrane transport properties measurement apparatus will also continue with emphasis on the further development of probe molecules and the production of the multicell apparatus.

The NIST Mass Spectral Database: Extending the Evaluation

CSTL Program: Chemical and Biochemical Data

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Abstract: While the growth of mass spectrometry in the last few years has been dramatic with instruments finding increasing use for more and different types of analysis, classical electron ionization (EI) with the use of gas chromatography/mass spectrometry (GC/MS) remains the principal analytical tool for organic analysis. The NIST Mass Spectral Database is the most widely used database for GC/MS analysis. New data for retention indices of a large number of chemicals are being added to ensure that the NIST MS Database continues to fulfill the needs of the organic analytical community. At the same time, algorithms are being developed so that the data can be used to assist data analysis in newer, rapidly advancing techniques such as MS-MS.

Purpose: The determination of the identity of a compound is a central problem in chemistry. For volatile substances, the most widely used, sensitive and definitive “fingerprint” for making such identifications is the electron-ionization mass spectrum. In practice, identifications begin with automated mass spectral “library searching” against a comprehensive library of reference spectra. The reliability of such identifications depends directly on both the quality of the reference library and the algorithms for matching mass spectra. The goal of this program is to provide a fully evaluated mass spectral database with tested and documented search algorithms to enable the reliable identification of unknown organic compounds by gas chromatography/mass spectrometry (GC/MS). The development of this library and search capabilities to the standards expected of NIST is a major challenge given our current inability to predict mass spectra along with unavoidable instrument- and compound-dependent variations in these spectra.

Major Accomplishments: Over the past year, evaluation has been completed for all spectra received since the previous release. No changes were made without agreement by at least two evaluators. The analysis was always conservative; if a given spectrum or spectral feature was not clearly in error, it was not changed. A significant effort has also been devoted to improving the consistency of chemical names and chemical structures. The accuracy of Chemical Abstracts registry numbers has been thoroughly established with the assistance of the Chemical Abstracts Service. Ongoing work on algorithm development has served to aid in the evaluation and to assist users of the NIST library in extracting structural information from the library. Work on new algorithms for searching of MS/MS spectra has been coupled with new efforts at determining MS/MS spectra for a variety of well known conditions in order to test the algorithms.

Impact: The NIST MS database is the most widely distributed mass spectra database in the world. Annual sales are over 2500 units, which represents about one-half of the GC/MS instruments sold world-wide. The database and its associated fully tested software are increasingly becoming the standard for industrial use. The database is used in drug discovery screening, drug testing, forensic analysis, pesticide and pesticide residue testing, as well as in numerous industrial quality control and product development labs. The extension of the

algorithms to prediction of MS-MS results will allow the electron impact database, by far the largest set of data in mass spectrometry, to be used by new, alternative ionization techniques. These methods have not been standardized to the extent that electron impact has; as a result, there is a far greater need for data coupled with algorithms that compensate for the different ionization source.

Future Plans: Work is continuing on the addition of retention indices to the database. The retention index is a measure of the time it takes a compound to elute from the gas chromatographic column. Use of retention information along with spectral matching significantly decreases the risk of false positive identification, especially for compounds not having highly unique spectra. Tools are being developed for both evaluation and estimation of retention index data and their uncertainties when direct determinations are not available. The role of MS-MS data and algorithms is also being extended. New instrumentation has been acquired to allow other ionization methods to be examined and to extend the data set for use in testing and refining the algorithm. Finally, algorithms designed to discover likely errors in mass spectral libraries are being developed to assist spectral evaluation.

Automated Gas Chromatography/Mass Spectral Decomposition and Analysis: Tools for Automating and Improving the Use of GC/MS Instruments (AMDIS)

CSTL Program: Chemical and Biochemical Data

Authors: *S.E. Stein, O. Toropov (Contractor), J. Reed, and W.G. Mallard*

Abstract: NIST has developed a tool for automatically analyzing gas chromatographic - mass spectrometric (GC/MS) data files - Automatic Mass Spectral Deconvolution and Identification Software (AMDIS) with the support of the Defense Threat Reduction Agency (DTRA) to determine whether chemical weapons banned under the Chemical Weapons Convention (CWC) are present in analyzed samples. AMDIS has subsequently been widely distributed by instrument manufacturers to aid their users in analyzing GC/MS data from complex mixtures. AMDIS can resolve close coeluting peaks, extract very small peaks from noisy backgrounds, and do so better and faster than could be done manually by an analyst. In addition to the ongoing work on improvements in AMDIS, technical assistance to the U.S. Delegation to the Organization for the Prohibition of Chemical Weapons (OPCW) is also provided in this project.

Purpose: This program was originally supported by DTRA to provide a method for determining whether chemical weapons banned under the CWC are present in samples analyzed by GC/MS. In order to insure that any proprietary or national security information not be revealed during the analysis, this had to be implemented without the operator examining the data. The resulting software allowed the data to be analyzed more quickly and without operator bias than had been possible with manual analysis. In addition, for a complex chromatographic region the overlapping components cannot be properly treated using manual "background subtraction." The exact deconvolution combined with the noise analysis provides a tool that is capable of providing more sensitive detection and of resolving components that are more closely coeluting than had been possible. All of these developments have been extended for use in the broader organic analytical community. In addition, direct support to United States treaty efforts are supplied by NIST within this effort. These include evaluation of data for use in inspections, consultation with United States representatives to the treaty organization on technical issues related to sampling and analysis, and direct assistance to U.S. inspection personnel.

Major Accomplishments: During the past year there has been a number of improvements in the software; these have included a fully functional DLL for use by instrument companies in conjunction with their own software and numerous improvements in the functionality of the software in response to user requests. The algorithms have been modified to allow for the specific noise characteristics of the instrumental noise in ion-trap mass spectrometers. In addition, a large body of data relevant to the detection of chemical weapons materials has been taken under contract in this program. The data have been extensively analyzed, and much of the resulting information will be released in the next NIST MS database. There is also ongoing work on the evaluation of data for addition to the OPCW database. This database is to be used for inspections at industrial and military sites and its accuracy is important. Ongoing technical support for the U.S. delegation to the OPCW has been provided.

Impact: The AMDIS package has been widely adopted by GC/MS instrument companies. Both the complete software package and the DLL have been adopted by various instrument companies.

AMDIS is currently in use for on-site inspections by the OPCW, and it is increasingly being accepted by the member states of the OPCW as the reference standard for their own work. In a small but significant way, the work at NIST is helping to reduce the chance of chemical weapons being used. By providing a way for the chemical industry of the world to undergo inspections without risking the loss of confidential business information, AMDIS is making the implementation of the Chemical Weapons Treaty easier and more effective.

Future Plans: Ongoing work involving the addition of reference data to the OPCW database and support for the United States Delegation to the OPCW will continue. In addition, the analysis of additional CW related data files will be performed to further test the algorithms in AMDIS. Since algorithms have been highly optimized over several years, remaining problems arise due to uncertainties inherent in the data. Future improvements in AMDIS are guided by user requests for increased functionality in both the complete software package and in the associated DLL. An important area for improvement over the next year is the improvement in the quantitative analysis of GC/MS data files. In a small number of cases, specific noise related problems with instruments can be identified and corrected. For these cases, improvements in the underlying peak detection algorithms may be possible.

The NIST WebBook* - NIST Chemical Reference Data for Industry

CSTL Program: Chemical and Biochemical Data

Authors: *W.G. Mallard, P.J. Linstrom, and D.H. Frizzell; and J.F. Liebman (University of Maryland – Baltimore County)*

Abstract: The NIST Chemistry WebBook continues to be one of the most widely used resources for chemical and physical property data in the world. Usage has continued to grow at about 20% per year with over 350,000 distinct IP addresses accessing the WebBook in the last year. Between 40% and 50% of these users are return users indicating a high level of satisfaction with the resource. Extensive additional vapor pressure data originating from the Thermodynamics Research Center have been added this year. Other recent additions include new high precision data for industrially important fluids and new calculational modules to allow transport properties from the equations of state for the fluids.

Purpose: There is an enormous amount of published thermochemical data (heats of formation, entropies, heat capacities, heats of reaction) as well as thermophysical property data (vapor pressure, viscosity, boiling points, melting points, etc) that are effectively unavailable to the technical community. One goal of this project is to find, transcribe and evaluate those data. The second part is to make this and other data such as infrared (IR), ultraviolet (UV) and mass spectra available and easy to access. The WebBook is being used by a very wide variety of users in industry, government, and academia.

Major Accomplishments: During FY01 the seventh edition of the NIST Chemistry WebBook* was released. The total number of compounds for which data are provided has increased so that properties for more than 40,000 compounds are available. New calculational tools were added to give access to more high precision fluid properties - a number of transport properties can now be calculated and 17 new fluids were added. A subset of the Thermodynamic Research Center data has been added which has especially broadened the coverage of vapor pressure and boiling point data sets.

Impact: Usage of data in the WebBook continues to increase – during FY01, the total number of distinct internet addresses that accessed the WebBook was in excess of 350,000. Growth in usage has been fairly steady from year to year – with same period usage increasing by about 20% in each of the last four years. The numbers of users, between 10,000 and 20,000 per week, and the variety of users, in industry, government and academia is a clear indication of the success of the WebBook. The fraction of returning users, typically between 45 to 55%, is a good indication that the user community feels that the resource is valuable. The WebBook is also a tool to aid future evaluation projects both at NIST and in collaboration. Collaborations with groups from Colorado School of Mines, Gaussian Inc, Exxon-Mobil, DuPont Chemical, and Reaction Design, Inc., as well as a number of other academic partners, have begun to allow the resources of the WebBook to be directly accessed by other computer programs used in problem-solving desktop environments by chemical engineers.

Future Plans: The goal of the WebBook is to have a single point of entry for access to all chemical data at NIST and to make that data available in formats needed by both individual

scientists and engineers as well as by computer tools serving these users. It is anticipated that during FY2002, there will be one or two releases of the NIST WebBook. The focus of the coming year will be on providing better automated access to the WebBook; additional data will also be added. In the longer term, it is anticipated that all TRC data will be available through the WebBook

*<http://WebBook.nist.gov>

Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation

CSTL Programs: Physical Property Data, Chemical and Biochemical Data

Authors: *M. Frenkel, R.D. Chirico, Q. Dong (Contractor), X. Yan (Contractor), X. Hong (Contractor), V. V. Diky (Guest Researcher), G.R. Hardin, and R.A. Stevenson*

Abstract: The new concept of “dynamic” data evaluation has been developed at TRC. This concept requires the development of large electronic databases capable of storing essentially all the ‘raw/observed’ experimental data known up-to-date with detailed descriptions of the relevant metadata and uncertainties. The combination of these electronic databases with artificial intellectual (expert-system) software designed to automatically generate recommended data based on available ‘raw/observed’ experimental data leads to the ability to produce data compilations dynamically or ‘to order.’ This concept contrasts sharply with static compilations, which must be initiated far in advance of need. Dynamic compilations dramatically reduce the effort and costs associated with anticipating future needs and keeping static evaluations current. The recommended data produced by the deployment of the dynamic data-evaluation concept can rigorously be characterized with their quality assessments providing the ability to propagate reliable data-quality limits to all aspects of chemical process design. The TRC Data Entry Facility was established in 2001 to support a mass-scale data entry operation for the TRC SOURCE data system. The new Data Quality Assurance Program has been designed to control the data quality at various stages of data entry, evaluation, and database management. The TRC Consortium has been established with six major companies participating.

Purpose: Thermophysical data evaluation is currently one of the most time- and resource-consuming stages of process design in a number of industries (chemical, petroleum, pharmaceutical, *etc.*). It also has very significant implications in the analysis of mutual relations of various properties within particular classes or groups of chemical substances, which is traditionally a subject of fundamental research. However, the unprecedented growth of thermophysical data becoming available at present (almost doubling every 10 years) makes it practically impossible to employ traditional (static) methods of data evaluation used over the last 50 years. The main objective of this project is to create new efficient methods and computer tools for thermophysical and thermochemical property data collection, critical evaluation, mining, quality control, management, and dissemination and to provide high quality recommended data in the forms directly suitable for industrial and scientific applications.

Major Accomplishments: The TRC Data Entry Facility was established in 2001 to support a mass-scale data entry operation for the TRC SOURCE data system. ‘Raw’ experimental data entry files will be coming primarily from four major sources: submission through major property-data periodicals, deliverables from outside contributors to the *TRC Tables*, international data collection projects which provide data either not readily available or published in non-English periodicals, and an extensive in-house student-based data-entry operation. The TRC Data Entry Facility represents a unique data collection operation having no parallel anywhere in the world. The new Data Quality Assurance Program has been designed to control the data quality at various stages of data entry, evaluation, and database management. The TRC Consortium has been established with six major companies participating.

Impact: The establishment of the TRC Data Entry Facility and TRC Data Quality Assurance Program will dramatically increase the TRC capabilities in volume and quality of the 'raw' experimental data collection, forming a necessary data management foundation for the implementation of the dynamic data evaluation concept. The recommended data produced by the deployment of the dynamic data evaluation concept will rigorously be characterized with their quality assessments providing the ability to propagate reliable data-quality limits to all aspects of chemical process design, which will have enormous economic impact across a broad range of industries.

Future Plans: The principal features of a Windows-driven interactive Guided Data-Entry Program will have to be formulated to ensure that all relevant information is captured and that proper formatting requirements are met in the preparation of the batch data entry files. The implementation of these features in the software product is planned to be done in the near future.

Measurements, Modeling, and Database Development for Supercritical Fluids and Alternative Solvents

CSTL Program: Physical Property Data

Authors: *T.J. Bruno, A.F. Lagalante, and W.C. Andersen; and A. Abdulagatov (Dagestan Scientific Center of Russian Academy of Sciences)*

Abstract: Safe replacements for toxic solvents come from fully or partially fluorinated alkanes, ethers, or ketones with negligible ozone depletion potential, as well as functionalized glycol ethers and siloxanes. The most important thermophysical parameter required to assess the feasibility of a solvation process is the solute-solvent phase equilibrium. Serious limitations exist in equation-of-state (EOS) approaches that use only solute/solvent physical properties to model phase equilibrium in alternative solvent systems, due to solution nonidealities. Many of the fluorinated alternative solvents are gases under ambient conditions, and their thermophysical properties offer the promise of both conventional liquid extraction and the tunable solvent strength offered by near-critical and supercritical fluid extraction. In our approach, a solution process is modeled as the dependent variable in a multivariate analysis. The independent variables include solute-solvent interactions and state-dependent terms. Solute-solvent interactions are quantified using empirical solvatochromic and chromatographic parameters of acidity, basicity, polarizability, and polarity. These parameters represent the dominant chemical interactions in solvent-solute systems and account for contributions to the nonideal portion of phase equilibrium. Treating these interactions will permit higher accuracy than EOS approaches. The statistical model aids in the identification of alternative solvents by making it possible to predict the solubility of industrially relevant compounds.

Purpose: The objective of this work is to develop and test predictive models for solvation of compounds in alternative solvents at supercritical, near-critical, and subcritical conditions using a combination of both physical and chemical variables as input into an empirical multivariate statistical model.

Major Accomplishments: In recent years, we have designed and constructed numerous spectroscopic, chromatographic, and gravimetric instruments for the measurement of solubilities of solutes in subcritical and supercritical fluids. This includes a fiber-based solvatochromic sensor that uses UV-vis spectrophotometry. Solutes studied have ranged from organometallic compounds to physiologically active natural products. The solvatochromic properties that are measured are temperature dependent, and in the case of supercritical fluids, density dependent. This allows models to achieve a high level of flexibility. For example, we have modeled the partitioning of organic solutes in 1,1,1-trifluoroethane/water, 1,1,1,2-tetrafluoroethane/water, and carbon dioxide/water. In addition to the spectroscopic instrumentation, we have developed a new vapor-entraining rotor for supercritical fluid extraction of aqueous mixtures. This device dramatically improves the contact of a supercritical fluid with the aqueous phase. The new rotor has improved extraction efficiencies from 40 to over 90 percent.

Impact: As an example of the impact of this work, we have been able to demonstrate that solvation strength of the glycol ethers is maintained constant even in dilute aqueous solutions.

This has allowed production of solvent formulations of much lower cost, at no sacrifice in effectiveness. Also, our invention of the entraining rotor has improved aqueous supercritical fluid extraction efficiencies dramatically.

Future Plans: In the near future, we will extend the solvent work to include dissolved ligands as alternative solvents. Preliminary experiments with soluble crown ethers have already been started.

Publications:

Hansen, B.N., Harvey, A.H., Coelho, J.A.P., Palavra, A.M.F, and Bruno, T.J., ***Solubility of Capsaicin and Beta-Carotene in Supercritical Fluid Carbon Dioxide and in Halocarbons***, J. Chem. Eng. Data 46, 1054 (2001).

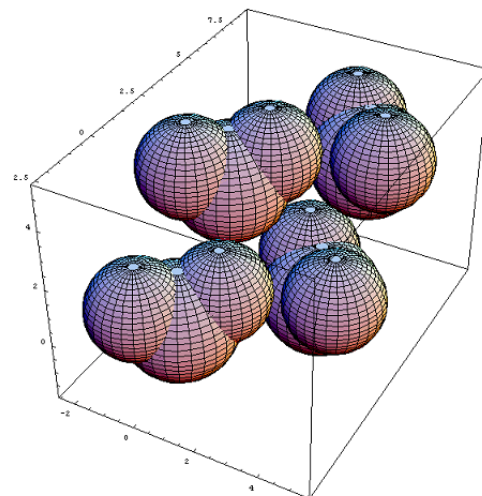
Andersen, W.C., Sievers, R.E., Lagalante, A.F., and Bruno, T.J., ***“Solubility of Cerium(IV), Terbium(III), and Iron(III) β -Diketonates in Supercritical Carbon Dioxide,”*** J. Chem. Eng. Data 46, 1045 (2001).

Solid-Liquid Equilibrium: Data and Models

CSTL Program: Physical Property Data

Authors: *J.C. Rainwater, and S.A. Kadlec; and P.D. Beale (University of Colorado)*

Abstract: Significant new developments have recently been made in the theory and prediction of the solid-liquid transition of molecular systems. Our focus is on molecules with a dipole moment, modeled as a fused hard-sphere system with mean-field attraction and electric multipole moments added as perturbations. We showed that methyl chloride, modeled as a diatomic molecule, freezes into a more open crystal structure than expected, seen experimentally, because of the dipole moment. Our current focus is sulfur dioxide, and we plan to progress to molecules with an increasing number of atoms or atomic groups. Liquid free energies are calculated by NPT simulations over a range of densities. We are investigating several methods for solid free energy calculation, including the simple cell model, an alternative fluctuating cell model, the standard Frenkel-Ladd method of simulation of a system at different spring constants, and a promising novel method in which the springs are attached intermolecularly rather than to points on a fixed lattice structure.



Unit Cell of SO₂

Purpose: For any industrial application employing liquids, it is important to know at what conditions of temperature and pressure a transition to a solid takes place. Traditionally, an understanding of the solid-liquid transition has lagged far behind that of the vapor-liquid transition, but new theoretical and computational developments are promising. Clearly, the solid-liquid transition, except in special cases, does not obey the law of corresponding states. Mixtures are also important, and while most often the mixture phase diagram has a simple eutectic structure, there are at least six different possible topologies of the binary phase diagram. In any computer package for a fluid equation of state, the solid-fluid transition is an essential boundary of the range of application of that equation of state, and must be at least estimated.

Major Accomplishments: Our specific current focus is the compound sulfur dioxide, as a prototype of a triatomic molecule with a substantial dipole moment. We have fully characterized the unit cell of the sulfur dioxide crystal, and have developed techniques employing quaternions for the rotational degrees of freedom of this molecule. This is a significant advance over our earlier studies of linear molecules, where now there are three instead of two angular degrees of freedom. In two dimensions, we showed, and published in *J. Chem. Phys.*, that the fluctuating cell model does worse than the simple cell model for hard disks, but better for hard dumbbells with any significant elongation. A similar result for hard spheres has been established in three dimensions, both by Monte Carlo integration and use of an exact analytic expression we have developed; the two approaches are in excellent agreement. Finally, we have developed a promising new technique for simulating the free energy of a solid, where we integrate over

spring constants but attach springs between molecules, instead of from the molecule to a fixed lattice site as is traditional. Our new method shows promise of enabling us to simulate much larger systems.

Impact: The database under construction for this project will collect known information on melting curves, Simon equation parameters, crystal structures, and mixture phase diagrams. This information will be incorporated into NIST standard reference databases, such as NIST14, as appropriate. The incorporation of validated solid-fluid boundaries and models into a NIST database will increase the utility of the information in the areas of chemistry, separations, and process engineering. The work will provide guidance to experimentalists in what to measure, as has already been the case for methyl chloride where x-ray diffraction studies in small pores were conducted by a Japanese laboratory.

Future Plans: Our immediate plans are to complete the full solid-liquid equilibrium calculation for sulfur dioxide and to test the three-dimensional fluctuating cell theory for hard dumbbells, where we expect, as in two dimensions that it will show improvement over the simple cell theory. We next plan to study the difference in freezing temperatures between normal and branched alkanes, starting with n-butane and isobutene. We also plan to conduct a fundamental study of mixtures, particularly those that do not form the simple eutectic structure. As our new method of calculating solid free energy with intermolecular springs is tested, we will, if appropriate, move toward larger system sizes and more elaborate molecules.

Workshop on Predicting the Thermophysical Properties of Fluids by Molecular Simulation

CSTL Program: Physical Property Data

Authors: *R.D. Mountain, A. Chaka, D.G. Friend, and R.D. Johnson III; and M.R. Nyden (866)*

Abstract: This workshop initiated a programmatic effort directed at stimulating further research in the development and validation of force fields and methods for molecular simulation of fluid properties that are industrially important. This effort is well aligned with the recommendations set forth in the Technology Vision 2020 exercise and the subsequent Technology Roadmap for Computational Chemistry. The workshop program focused on the needs of industry for predictive capabilities for thermophysical properties and on how those needs might be realized now and in the future as computational capabilities and molecular force fields improve. Molecular simulations have been extensively developed by specialists. It is time to transfer this methodology to industry for use by non-specialists. Working groups developed a series of recommendations on next steps to be implemented by the participants. Tutorials on methods will be developed. An open competition will be organized where method developers and simulation practitioners will be challenged to predict specific properties of molecular liquids. The properties will not be available in the open literature prior to the completion of the competition. NIST will coordinate the competition. A series of publications will be prepared to stimulate interest in the application of simulation methods to industrial needs. An industrial consortium will be organized to work with commercial and academic software developers to make simulation methodologies more widely available and acceptable for the prediction of fluid thermal properties.

Purpose: The workshop was organized to identify industrial fluid property prediction needs that could be satisfied using molecular simulation methods now or in the near future, and to help drive the research to ensure that molecular simulation will be a relevant, robust and reliable tool in the longer term. Barriers to the implementation and acceptance of simulation methods by non-full-time simulators were to be identified, and possible steps to achieve more widespread implementation and acceptance were to be developed. There was an emphasis on the development and validation of force fields and molecular simulation methodologies.

Major Accomplishments: Forty-two persons from industry (including Ford, Colgate-Palmolive, 3M, Rohm and Haas, GM, Bristol Myers Squibb, Exxon-Mobil, Union Carbide, DuPont, Dow, BP), government (NIST, PNNL, Sandia) and fifteen academic institutions participated in the workshop held at NIST-Gaithersburg on June 18-19, 2001. A list of industrial needs was developed. Working groups on tutorials, publications, a consortium, and a computational challenge competition were established. These groups are currently active, and information about the Workshop is available at <http://www.ctcms.nist.gov/~fstarr/ptpfms/home.html>.

Impact: A group has been established to coordinate and catalyze the research needed to promote industrial use of simulation methods to determine thermophysical properties of fluids in experimentally difficult or expensive environments. Through the series of tutorial that is planned, both industrial practitioners and researchers will learn fundamentals and best practices

in several general areas of molecular simulation. The publications currently in preparation will serve a similar purpose. The Workshop also formed the nucleus of a committee to establish an industrial consortium on molecular simulation; this consortium would help fund research in this area and ensure relevance to industrial requirements for property prediction tools. The open competition is being conducted to drive the development of transferable force fields and algorithms, and will help focus effort on the vital requirement of validation of techniques.

Future Plans: This activity related to the Workshop outcomes is just starting, but this will be integrated into ongoing programs in the areas of molecular simulation, development of force fields and algorithms, database efforts related to simulation, and property prediction for industrial needs. The first computational challenge will be announced in November 2001 with a submission date of Sept. 1, 2002. A two-day tutorial will be held at the Spring AIChE meeting. A series of publications on the opportunities and challenges for molecular simulation in industry are planned.

Development of Efficient Tools for Computational Kinetics

CSTL Program: Chemical and Biochemical Data

Author: *C.A. Gonzalez*

Abstract: In this project, a series of modules that compute rate constants as a function of the temperature have been implemented into a generic piece of software. Given its wide applicability, Canonical Transition State Theory (CTST) has been chosen as the standard method to compute rate constants. Tunneling corrections are calculated using the one-dimensional Wigner, Symmetrical Eckart, or Unsymmetrical Eckart approaches. A module that treats normal modes as hindered rotors has also been implemented. In addition, properties such as vibrational frequencies, heats of reaction, entropies, and partition functions are also computed. The program has been implemented in standard FORTRAN 77, and it has the capability of reading output files from one of the most popular quantum chemistry programs.

Purpose: The use of modern computational chemistry methodologies in the prediction of molecular properties has become increasingly popular mainly due to significant improvements in the algorithms and the advent of powerful computer resources. This is particularly true in the area of thermochemistry, where researchers in industry and academia perform quantum chemistry calculations on a routine basis. Despite this progress, the use of similar methodologies in computational kinetics has been slow. In fact, computational kinetics remains an obscure area being used most of the time by experts in the field. There is no doubt that the application of quantum chemistry calculations in the area of computational kinetics will have significant impact. In order for this to happen, however, it is critical that state-of-the-art methodologies be widely available to the scientific community. The main goal of this project is the generation of computational tools that will allow scientists and engineers to perform reliable studies of the kinetics governing gas-phase chemical reactions that might play an important role in various industrial processes.

Major Accomplishments: The computational kinetics tools discussed in this project have been implemented in a computer software package that has been used extensively by some researchers at NIST in order to study the kinetics and reactivity of hydroxyl radicals towards a series of halogenated organic compounds as part of an ongoing project leading to the development of "screening tools" for the environmental impact of these compounds. Theoretical studies on more than twenty molecules have been performed and the results reported in three different publications.

Impact: Beta-test versions of the program running on PCs and UNIX workstations have been distributed among scientists inside and outside NIST.

Future Plans: We are currently extending the capabilities of the program so that Variational Transition State Theory can be used for reactions characterized by low barriers, where CTST gives poor results. We are also improving the methodologies used in the calculation of tunneling corrections. In addition, we started the development of efficient algorithms that would enable the fast characterization of reactant rotational conformers that might contribute to the kinetics of the

reaction. More calculations using these tools are being performed on halocarbons and ethers with one and two carbons. Finally, we are planning to make all these tools publicly available in the near future.

Benchmark Reference Calculations of Excited State Transition Energies by Quantum Monte Carlo

CSTL Program: Physical Property Data

Authors: *J.A.W. Harkless; R. Manaa (Lawrence Livermore National Laboratory; and W.A. Lester, Jr. (University of California, Berkeley)*

Abstract: An investigation of the performance of various *ab initio* methods in estimating electronic transition energies, using the quantum Monte Carlo (QMC) method in addition to traditional basis set *ab initio* wavefunction methods was performed. A continuing study of atomic and molecular excited states will provide understanding of both the effort and error associated with various methods on the atomic and small polyatomic scales. Diffusion Monte Carlo estimates of atomic transition energies had an average error of 0.2 eV, while traditional *ab initio* calculations gave variable results, with the CCSD(T) method outperforming CCSD, B3LYP, and MP2. Excited state benchmarking studies can assist researchers in developing expectations of the performance of computational techniques on larger systems.

Purpose: When a proper description of a chemical system requires estimates of excited electronic state energies in addition to ground state energies, many traditional computational techniques fall short. The majority of methods available will only work properly for the lowest-lying state of a given spin multiplicity. Methods capable of estimating electronic excited states in general, without introducing new formalism, include configuration interaction (CI), complete active space self-consistent field (CASSCF), and quantum Monte Carlo (QMC). Because computational methods are becoming commonly used in the description and prediction of reactions, high accuracy descriptions of all species involved are critical for reactions that may proceed through excited electronic states.

Major Accomplishments: Twelve electronic transitions were selected to represent a cross section of relatively simple systems that could be treated by various methods and compared to experiment. In addition to QMC and CASSCF, several single-reference methods were used, where applicable: a generalized gradient approximation density functional (B3LYP), second-order perturbation theory (MP2), singly and doubly excited configuration interaction (CISD), and coupled cluster with single and double excitations and perturbative triple excitations (CCSD, CCSD(T)). The basis set methods were executed using the correlation-consistent series of basis sets. Only the QMC, CASSCF, and CI methods were applied to all twelve transitions.

For the QMC values, we found an average error of 0.2 eV relative to experiment, which is a significant improvement over other current methods. The basis set methods in general disagreed with experimental values, with the CCSD(T) method giving the best agreement among the single-reference results. B3LYP estimates were not significantly worse, and in some cases, better than CCSD. The CASSCF estimates benefit from their multi-reference character, and are capable of finding reasonable agreement with experiment.

Impact: This continuing study of molecular excited states will provide understanding of both the effort and error associated with various methods on the atomic and small polyatomic scales.

Such studies can assist researchers in developing expectations of the performance of computational techniques on larger systems.

Future Plans: We anticipate that calculating the excited states of NO will improve our understanding of the effort, accuracy, and insight to be gained from computational excited state studies. Ozone has long been identified as computationally challenging; it also has an unusual reactivity profile. We anticipate that calculating estimates of bond dissociation energies as well as excited state energies expected to lie below and near the dissociation limit will provide insight into the properties of ozone.

Simulations of Viscous Properties of the Lennard-Jones Fluid

CSTL Program: Physical Property Data

Authors: *A. Laesecke, and K. Meier (Guest Researcher; and S. Kabelac (University of the Federal Armed Forces, Hamburg, Germany)*

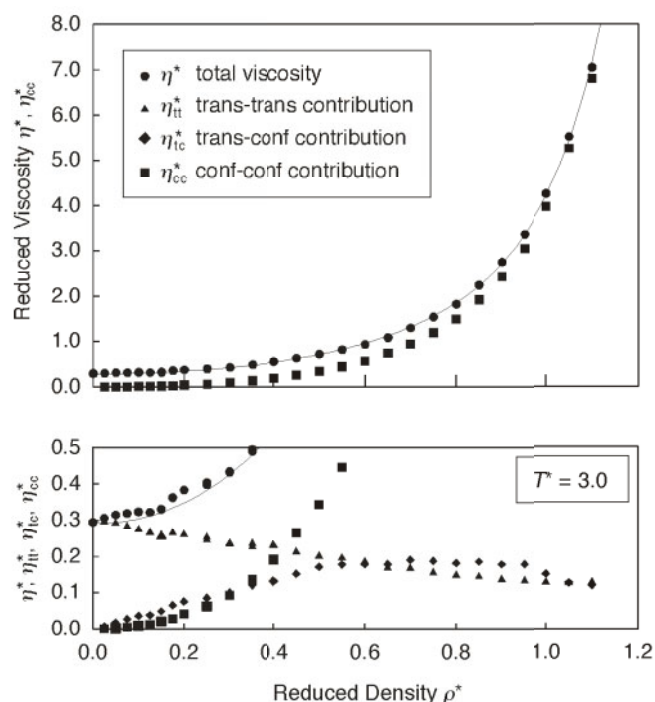
Abstract: Equilibrium molecular dynamics (EMD) simulations were carried out to determine the coefficients of self-diffusion, shear viscosity, and bulk viscosity of the Lennard-Jones fluid using the Einstein plot method. In this method, the transport coefficients were evaluated as the long-time limit of the slope of the mean-squared displacement corresponding to the transport property of interest. Over 300 state points were simulated covering the entire fluid region from the low-density gas to the compressed liquid near the melting line in the temperature range $T^* = T k_B/\epsilon = 0.7$ to 6 (4.5 times the critical temperature). Metastable superheated vapor and subcooled liquid states were also included. The simulations were performed with an ensemble of 1372 particles at constant $NV EP$ over 1.5 to 2 million time steps after initial equilibrations up to 300,000 time steps. The equations of motion were integrated using a step size of $\Delta t^* = 0.003$. The cutoff radius r_C^* was set to 5.0, 5.5, and 6.5, dependent on the density.

Purpose: Previous simulations with the Lennard-Jones potential model primarily targeted thermodynamic properties, while transport properties were largely ignored. Molecular dynamics simulations were needed to fill the gap.

Major Accomplishments: Transport coefficients for self-diffusion, shear viscosity, and bulk viscosity of the Lennard-Jones model fluid were determined with high precision *via* equilibrium molecular dynamics (EMD) simulations. Using more particles, larger cutoff radii, and much longer simulation times, significantly more accurate data were obtained than in previous studies. The uncertainties of the present results are conservatively estimated at ± 0.5 % for self-diffusion coefficients and ± 2 % for viscosities in the liquid region, increasing to ± 15 % or more at low-density gaseous states.

The subdivision of the shear viscosity into translational-translational, translational-configurational, and configurational-configurational contributions that arise naturally in the time correlation function formalism was resolved for the first time over broad ranges of fluid state conditions. An example of the density dependence of these contributions is shown in the figure along the supercritical isotherm $T^* = 3.0$.

A pronounced critical enhancement of the bulk viscosity was found. Unlike the critical enhancement of the shear viscosity, it is not confined to just a narrow region around the critical point. This previously unexplored behavior of the bulk viscosity can be interpreted in terms of pressure fluctuation autocorrelation functions. It turns out that the enhancement is caused by very slowly decaying pressure fluctuations.



In order to achieve near-experimental uncertainties of the transport properties, the simulations were carried out over much longer times than if we had focused only on thermodynamic properties. Conversely, the simulations yielded as by-product thermodynamic properties of the Lennard-Jones model fluid at unprecedented levels of uncertainty.

Impact: A goal of this project was to contribute to the development of standards in the area of molecular simulation. Thus, our simulations were carried out over broad ranges of state conditions with uncertainty levels that would be expected from experimental measurements. The simulations resulted in data that form a

sound basis for reference quality correlations of the properties of the Lennard-Jones model fluid.

The fact that we derived transport properties from equilibrium molecular dynamics simulations rather than from nonequilibrium measurements is likely to stimulate theoretical studies of the interrelation between thermodynamic and transport properties. Resolution of the three viscosity contributions η_{tt}^* , η_{tc}^* , and η_{cc}^* provides new insights into the nature of molecular transport mechanisms on the nanoscale.

Future Plans: This work represents a significant beginning in the development of standards for molecular simulations for the Lennard-Jones model fluid. Next, EMD simulations of thermal conductivity should be carried out. Future work will also include the Stockmayer potential, which has seldom been studied by molecular simulation.

Publication:

Meier, K., Laesecke, A., and Kabelac, S. “*A Molecular Dynamics Simulation Study of the Self-Diffusion Coefficient and Viscosity of the Lennard-Jones Fluid*,” Int. J. Thermophys. 22, 161 (2001).

Virial Coefficients for Aqueous Systems

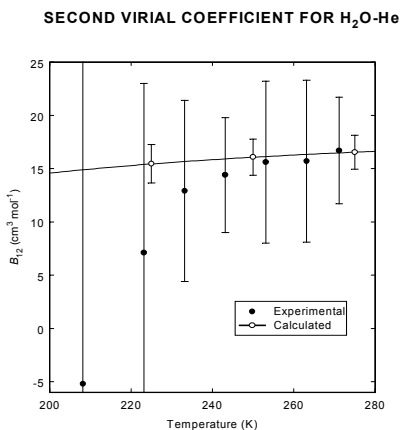
CSTL Program: Physical Property Data

Authors: A.H. Harvey, and J.W. Magee; M.P. Hodges, and R.J. Wheatley (University of Nottingham, United Kingdom)

Abstract: The thermodynamics of aqueous vapor mixtures is important in a variety of areas, from properties of combustion gases for the power industry to the improvement of humidity standards. An appropriate description for many of these systems is at the level of the second virial coefficient (first correction to the ideal gas). However, measurement of these water/gas second virial coefficients is difficult; where data exist, they have high uncertainties and are limited to a narrow temperature range. We have bypassed the experimental difficulties by constructing an intermolecular potential energy surface and using it to calculate the second virial coefficient directly from statistical mechanics. Work on the water/helium system has been completed, and for that system the uncertainty in our derived second virial coefficients is much smaller than for the limited data. We expect similar results for water/neon and water/argon, which are in progress. Ultimately, our aim is to complete calculations for water with air components and other species important in combustion environments, producing improvements in humidity standards and improved designs for industrial systems such as combustion turbines.

Purpose: A significant limitation in the accuracy of humidity standards is the description of the nonideality of the water/air vapor mixture. Current standards are based on some very difficult experiments with large uncertainties. The properties of moist air are also important in other metrology applications: for example, the refractive index is crucial for interferometry. In industry, properties of gases containing water are important in the heating, ventilation and air conditioning (HVAC) industries, in advanced power cycles utilizing humid air, and in the design of combustion systems. In all these cases, the conditions are such that an appropriate level of description is given by the second virial coefficient $B(T)$, the first correction to the ideal gas law. However, experimental determination of second virial coefficients for aqueous systems is difficult and prone to uncertainty, primarily due to adsorption effects. The few results that do exist only cover a narrow range of temperatures, when the need is for data at temperatures as low as 200 K (for humidity standards) and as high as 1500 K (for combustion applications).

Our approach is to calculate the second virial coefficient directly from statistical mechanics, which can be done rigorously at all temperatures of interest if a sufficiently accurate intermolecular potential is available. We develop potentials based on *ab initio* quantum mechanics, using a technique that saves computational effort by incorporating a limited number of highly accurate super-molecule calculations to calibrate the results of intermolecular perturbation theory.



Major Accomplishments: A potential energy surface was derived for the water/helium system and used to calculate second virial coefficients. As shown in the figure, the resulting values of $B(T)$ agree with the limited

experimental data available, but have much smaller uncertainties and are not limited to a narrow temperature range. This work is in press in *J. Chem. Phys.* A potential energy surface and second virial coefficients have been derived in a similar manner for water/neon. For that system, there are no data with which to make comparisons. Work is well underway for water/argon.

Impact: When complete, this work will improve metrology, particularly in the area of humidity standards, by providing a more accurate description of water/air mixtures. In addition to the benefits afforded by better standards, industry will be better able to design processes (such as those involving combustion turbines) that involve aqueous gas mixtures.

Future Plans: After finishing the water/argon calculations, we plan to move on to systems with diatomic gases. Development of potential-energy surfaces for these systems is more challenging due to their additional degrees of freedom, but it is becoming feasible with advances in computing technology. The major species of interest would be H_2 , N_2 , and O_2 , with CO and CO_2 as possible additional targets. In addition, we plan to use a new apparatus now under construction to validate our calculations by taking pressure-volume-temperature data (from which second virial coefficients may be derived) for water with some of these gases at temperatures from approximately 500 K to 800 K.

Aircraft Fuel Tank Safety: An Application of Thermophysical Properties Modeling

CSTL Program: Physical Property Data

Authors: *M. Huber; and J. C. Yang (866)*

Abstract: Fuel storage vessels often contain multiphase mixtures of air, fuel vapors, and liquids; the compositions and properties of these phases are key data required to understand and optimize safety features in a variety of situations. As a prerequisite to a comprehensive analysis of aircraft fuel tank fire and explosion hazards, a vapor-liquid equilibrium thermodynamic analysis was developed to assess the fuel vapor behavior in an aircraft fuel tank ullage. The analysis was based on the Peng-Robinson equation of state and the extended corresponding-states method. Jet-A fuel was treated as a pseudo single-component fluid and as a binary mixture.

The calculated fuel/air mass ratios from the binary-mixture model followed the trend observed in previous measurements more closely than those from the pseudo single-component model. The calculated results also demonstrated that for a given amount of fuel, increasing the tank temperature could potentially cause an initially non-flammable fuel/air vapor in the ullage to become flammable.

Purpose: The safety of fuel storage vessels depends, in part, on the flash point temperature of the fluid in the vapor phase. The U.S. National Transportation Safety Board concluded that the probable cause of the fatal accident in TWA Flight 800 (7/17/96) was the ignition and subsequent explosion of vapors in the center wing fuel tank. The problems of fire suppression and related safety issues in fuel tanks, especially those certified for aircraft use, have never been studied using rigorous thermodynamic models with an adequate experimental database. Currently, safety considerations are determined using idealized models which may not capture some of the essential features involved with the compositions and properties of the fuel tank ullage, which are functions of fuel composition, initial loading, temperature, tank volume, fuel consumption, venting, etc. We have performed a thermodynamic analysis of the vapor-liquid equilibria in a system containing jet fuel and air.

Major Accomplishments: The primary focus of our initial study has been on the effect of fuel mass loading in the tank on the fuel vapor concentration in the ullage. The thermodynamic study considers a fuel tank with a given volume charged with a known mass or volume of fuel at a specified temperature and pressure. The fuel vapor concentration and the mass ratio of fuel to air in the ullage are then calculated from the thermodynamic models. Although Jet-A is a complex mixture of hydrocarbon fluids, we have followed standard procedures in considering a pseudo-pure fluid with averaged properties and a binary mixture (of normal nonane and normal decane). The calculations were based on a Peng-Robinson equation of state and an extended corresponding states model. Comparisons were made with the very limited experimental data that are available. The thermodynamic calculations were shown to capture the fuel vapor behavior in the ullage, and this method provides the possibility for a more detailed understanding



TWA800 fuselage
reconstruction

of phase partitioning and safety considerations. A manuscript describing these results has been submitted for publication in the Fire Safety Journal.

Impact: This project presents an example of the use of validated thermodynamic models to address a wide variety of problems. The specific collaboration between NIST experts in fire research and physical property data arose with the realization that the existing models for fuel tank ullage properties are somewhat primitive. A more complete model of such systems may lead to regulations concerning inerting of the vapor phase, venting requirements, consumption guidelines, fuel formulation, *etc.* These would directly relate to aircraft safety, and, perhaps, more generally, to improved guidelines for the storage and transportation of hydrocarbon or other fluid fuels. Such regulations, guidelines, or innovations cannot be rationally achieved without a careful consideration of the thermophysical properties of the fluid phases.

Future Plans: Several other specific issues in the area of aircraft safety are being considered as continuations to this research program. The question of inerting of the vapor phase may be addressed by examining properties of mixtures of fuels (and air) with the various agents. Additional modeling of the fuel tank ullage, relaxing the assumption of a closed system (and thus considering dissolved air, fuel evaporation, venting, and consumption), may also be attempted. Finally, we mention that fuel properties and formulations remain as important issues for which validated thermodynamic considerations may be applied.

Exploring Reaction Kinetics and Physical Properties of Ionic Liquid Systems

CSTL Programs: Physical Property Data, Chemical and Biochemical Data, Environmental Measurements

Authors: *D. Behar, P. Neta, J. Magee, and M. Frenkel; and G. Kabo (Belarusian State University, Minsk, Belarus)*

Abstract: Ionic liquids, a class of organic salts that are liquid at room temperature, have been proposed as new “Green Solvents” for various industrial applications. In spite of many advantages that these liquids offer, fundamental data on their physical and chemical properties are scarce. We have begun to study the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions. Published and unpublished physical properties measurements are being compiled and evaluated, and experimental measurements have been initiated on ionic liquids representing broad classes of compounds. Rate constants for several oxidation and reduction reactions in ionic liquids were measured by pulse radiolysis and found to be lower than rate constants for the same reactions in water and close to those in some organic solvents. The low rate constants are partly due to the high viscosity of these solvents limiting the diffusion rate. For reduction reactions involving solvent radicals, however, the rate constants were much higher than the diffusion-controlled limit and suggest an electron hopping mechanism.

Purpose: The physical properties of ionic liquids may be tuned, for example by altering the hydrophobicity, and this affects solubility, reaction rate, and selectivity. In spite of the many advantages that ionic liquids are predicted to offer, fundamental data on their physical and chemical properties are scarce. To provide U.S. industry with the knowledge base to exploit these solvents, we have begun to study the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions.

Major Accomplishments: A physical properties database is being developed that will provide industry with access to evaluated physical property data, validated models to interpolate the available measurements, and structure-property tools to predict physical properties not yet measured. It is becoming clear that measurements are scarce for most physical properties. We have initiated experimental measurements with a focus on five physical properties – density, heat capacity, vapor pressure, viscosity, and thermal conductivity. A preliminary study has shown that the choice of either the cation or the anion strongly influences the physical properties of the ionic liquid. We will explore the effects of length of the alkane side-chain attached to the cation, which has a rather bulky, asymmetric alkane-based structure that accounts for the low-temperature freezing points. The influence of the anion on physical properties is also very strong and will be explored by selecting three anions $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ for experimental studies

Rate constants for several oxidation and reduction reactions in ionic liquids were measured by the pulse radiolysis technique and compared with the rate constants for the same reactions in other solvents. Oxidation was probed by the reaction of the trichloromethylperoxyl radical with two typical organic reductants, a phenothiazine and a phenol. The rate constants in several ionic liquids are much lower than those determined in aqueous solutions and close to those measured

in low-polarity organic solvents such as ethanol, suggesting a high degree of ion association in the ionic liquids. On the other hand, the activation energies of the reactions are close to those measured in aqueous solutions but higher than that in alcohols. Moreover, when the rate constants in each solvent are compared to the diffusion-controlled limits estimated from the viscosity of the solvent, it is found that in both water and the ionic liquids, the experimental rate constants are close to the diffusion limit, whereas in alcohols and other organic solvents, the experimental values are much lower than the diffusion limit.

Rate constants for several reduction reactions were found to be lower in ionic liquids than in water or alcohols. The rate constants are close to the diffusion-controlled limit in ionic liquids and in water but much lower than the diffusion limit in alcohol. Interestingly, reduction of various compounds by a pyridinyl radical derived from a pyridinium ionic liquid took place considerably more rapidly than the diffusion-controlled limit, suggesting electron hopping through solvent cations. In reduction reactions involving two solutes (methyl viologen and quinones), the ionic liquid also affects the relative reduction potentials of the two redox couples and this leads to great changes in rate constants (by four orders of magnitude in one case) or even to reversal of the direction of the reaction.

Impact: This project will provide industry with essential data on physical properties and reaction kinetics to help accelerate the development of industrial processes that exploit the unique properties of ionic liquids.

Future Plans: Structure-property relationships for physical properties will be explored by analyzing evaluated data in our database. Based on the measurement trends that are found in the data, a group-contribution correlation will be developed for each key physical property to serve as a guide for future work in this area.

Rate constants for additional types of reactions will be determined, e.g., addition and abstraction reactions. Preliminary experiments also show that ionic liquids may be better than organic solvents for the preparation and stabilization of colloidal metal particles, which can serve as catalysts for various reactions. This aspect of ionic liquids will also be explored.

Fifth International Conference on Chemical Kinetics

CSTL Program: Chemical and Biochemical Data

Authors: *J.W. Hudgens, and R.E. Huie*

Abstract: CSTL's Physical and Chemical Properties organized and held the Fifth International Conference on Chemical Kinetics in early summer, 2001. This was the fifth in a series of quadrennial conferences designed to bring together scientists from different areas that have a common interest in chemical kinetics, both in the gas and liquid phases. These scientists include both those who generate and those who use chemical kinetics data. This utilization of chemical kinetics is predominantly in the modeling of complex chemical processes. Important examples include the models of the stratosphere that underlie the phase-out of halocarbons, models of urban air pollution, and models of chemical vapor-deposition processes. Kinetic models are now being developed to allow the modeling of soot formation and, ultimately, its control. The conferences in this series are designed not to focus specifically on a single problem to which chemical kinetics is applied. Rather, the goal was to have a much wider ranging conference where practitioners and users of chemical kinetics would be exposed to more diverse information, so that they could draw upon much more of the wealth of the field.

Purpose: Chemical kinetics is a fundamental tool for the understanding and control of complex chemical processes, both directly by providing rate data on the elementary reactions involved, and indirectly by an improved understanding of the reactivity patterns and the thermodynamics of reactive intermediates. Many reaction types and intermediates are of key importance in a number of different areas and under widely different conditions. Often, investigators in one field are unaware of studies carried out in another field, which may provide useful insights. This is particularly true if different physical phases are involved. Thus, broadly based meetings are needed periodically to bring together disparate members of the kinetics community.

Major Accomplishments: The conference was held July 16-20, 2001 and attended by 150 scientists from all parts of the globe. There were 60 oral presentations, which included five invited talks, and about 120 poster presentations. Oral sessions took place in the Red Auditorium at NIST and poster sessions were held at a local hotel, which provided an atmosphere conducive to personal interactions. Session topics were on Modeling, Radical-Radical Reactions, Unimolecular and High-Pressure Kinetics, Condensed Phase Kinetics, Atmospheric Chemistry, Ion and Plasma Processes, and Combustion Chemistry. A special session on Small Radical Chemistry and Photochemistry was held to celebrate the career of Hideo Okabe. The Conference was also served by a World-Wide-Web site, through which conferees could obtain information about the conference, could register, *etc.* The abstracts, which were submitted by e-mail, were converted to HTML format and all abstracts for the meeting were posted on the web site and available to all of the conferees well in advance of the conference. The file of conference abstracts could be searched by key word or by author, and an Acrobat file was also available for downloading. The web site also had links from the oral sessions to topical posters, to better integrate the poster presentations with the oral program. The entire program, with abstracts, can be found at: <http://nist.gov/kinetics/>.

Impact: This broadly based conference has filled a major need in the kinetics community. It has allowed cross-fertilization across the field and the integration of results from various sub-disciplines.

Future Plans: All of the oral presentations at the Conference were recorded. With the permission of the speakers, we intend to combine these presentations with the speakers' slides in order to prepare a webcast. This will allow participants and others to view the presentations over the World Wide Web. In future conferences, this may lead to real-time webcasts of the conference.

Thermochemical and Chemical Kinetics Data for Organometallic Compounds

CSTL Programs: Chemical and Biochemical Data, Microelectronics

Authors: D.R. Burgess, Jr., J.W. Hudgens, and E. Hunter

Abstract: Organometallic compounds are used during manufacturing processes to deposit metals in semiconductor, optical, fuel cell, MEMS, and NEMS devices. The thermochemical properties and reaction kinetics of most useful organometallic compounds and related molecular precursors are poorly characterized. This project obtains these properties through three activities involving theoretical estimations and laboratory measurements. The first data activity, which is in coordination with the Standard Reference Data Program, compiles and evaluates currently available thermochemical data of organometallic compounds and related precursors. This data will become available through an external NIST website. The second activity supplements available data by using *ab initio* and semi-empirical calculations to develop reaction mechanisms from computed molecular structures, thermodynamic properties and spectroscopic properties of Group III and Group V compounds. The third activity is a laboratory measurement program that measures the thermal decomposition kinetics of organometallic compounds. Each measurement series produces Arrhenius-like equations describing homogeneous and heterogeneous decomposition rates as a function of temperature.

Purpose: By using advanced measurement and computational facilities, this project measures, estimates, and disseminates fundamental thermochemical and chemical kinetic properties of organometallic compounds, facilitating the design and enhancing the safety of processes used to fabricate semiconductor, optical, fuel cell, MEMS, and NEMS devices.

Major Accomplishments: A prototype internal website is under development (<http://h105097.nist.gov/ckmechx/>). This site currently contains thermochemical and bibliographic information of silicon hydrides and halocarbons important to semiconductor processes. Thermochemical and spectroscopic data for Group III and Group V hydrides have been compiled, including stable molecules and radicals. These properties are compared to *ab initio* results. Bond dissociation energies (BDE's) for the indium methyl hydrides $\text{InH}_x(\text{CH}_3)_y$ have been computed, as well as transition state calculations for relevant reactions such as abstraction of H atoms from the indium methyl hydrides (In-H, CH_2 -H bonds) by H atoms and CH_3 . A simple decomposition mechanism has been constructed based on these data. A turbulent/laminar flow apparatus for thermodecomposition kinetic rate measurements of organometallic compounds was designed and constructed. The kinetic apparatus resides in a standing hood facility and consists of a heated flow reactor, flow controllers, and a Fourier-transform infrared spectrometer. In this facility experiments measure decomposition yield as functions of temperature and flow velocity. By fitting decomposition data to a kinetic model, homogeneous and heterogeneous thermal rate equations are derived. To validate apparatus accuracy, a series of calibration experiments involving the thermal decomposition of di-t-butyl peroxide were performed.

Impact: These activities will enable CSTL to provide reliable fundamental kinetic data of organometallic compounds, fulfilling data needs of the chemical vapor deposition (CVD)

equipment manufacturers. Since CVD precursor use continues to grow rapidly within several industries, we expect that the demand for these data will also increase.

Future Plans: Future plans include additional data acquisition, computations, and dissemination activities. After improvements are implemented and content is reviewed, the internal website devoted to organometallic materials will become public. The research will expand to include *ab initio* calculations leading to estimates of thermochemical properties for copper and aluminum compounds. Experiments will provide homogeneous and heterogeneous Arrhenius-like decomposition equations of selected volatile organometallic compounds composed of metals (Cu, Ga, Al, In, Pt, Zn...) and ligands (alkyl, allyl, tfac, NMe_n ...).

Thermal Decomposition of Chlorinated Hydrocarbons: Testing the Evaluations

CSTL Program: Chemical and Biochemical Data

Authors: J.A. Manion, I.A. Awan (*Guest Researcher*), D.R. Burgess, Jr., and W. Tsang

Abstract: Rate constants for the decomposition reactions of chlorinated hydrocarbons are measured at temperatures near 1000 K using single-pulse shock tube studies. Our objective is to test our recently proposed changes to heats of formation of highly chlorinated compounds, as well as resolve contradictory information on the kinetics of these compounds. These data are needed in models of industrial production and destruction of these compounds, as well as in assessing their environmental fates. In addition, *ab initio* computational studies are carried out to extend the range of compounds for which reliable information is available.

Purpose: Chlorinated hydrocarbons are widely utilized throughout the chemical industry, both as end products and as precursors for a wide variety of useful products, including plastics, solvents, pesticides, refrigerants, and other products. Attempts to understand and model the chemistry associated with the production, disposal, and environmental fates of chlorinated materials require that reliable kinetic and thermodynamic values are available for these compounds. Our recent evaluations have brought to light some existing problems with both kinetic and thermodynamic data, and we have suggested some significant changes to currently available values. If correct, these changes have important implications regarding the chemistry of these compounds. Additionally, a major current thrust is to develop computational methodologies enabling the rapid prediction of key physical properties. Species of interest frequently have highly polar substituents, including chlorine, and these compounds have proved to be among the most difficult to calculate accurately. It is therefore extremely important to have a reliable database with which to compare alternate predictive strategies. The present challenge is to devise and carry out experiments that will provide substantive tests of key issues resulting from our kinetic and thermodynamic data evaluations.

Major Accomplishments: From our data evaluations, among the most significant results were proposed changes to the enthalpy of formation values of highly chlorinated compounds, including hexachloroethane, pentachloroethane, and tetrachloroethene. We have subsequently measured the thermal decomposition rates of hexachloroethane and eight other chlorinated C₂ and C₃ hydrocarbons utilizing the shock tube methodology. In the case of highly chlorinated species, these studies provide direct information on carbon-carbon and carbon-chlorine bond energies. The presently obtained pressure and temperature dependent kinetic information can be combined with literature data to obtain a picture of the thermal decomposition behavior of the species in question over a wide range of conditions. Analysis of the data using ChemRate, a sophisticated RRKM modeling package developed at NIST, provides a narrow bounds of acceptable thermodynamic values that are consistent with the kinetic data and hence serves to test our evaluations. Our experimentally observed product distributions and decomposition rates of C₂Cl₆ could not be reconciled with older thermodynamic values, but are in very good agreement with the newly proposed data set. Results on the thermal decomposition of pentachloroethane also confirm the correctness of the new values. Additional kinetic studies of the pressure dependence of molecular HCl elimination from a series of other chloroethanes were

undertaken and have resolved the contradictory information on this reaction class. Parallel with the above experimental work, we have completed a series of computational studies aimed at improving predictive capabilities for both reaction kinetics and thermodynamic properties of this class of compounds.

Impact: These studies have tested and ultimately supported our recently proposed changes to the heats of formation of highly chlorinated hydrocarbons. This information will allow the development of more accurate models of the industrial production, disposal, and atmospheric fate of this important class of compounds. More generally, this information provides computational chemists with crucial benchmark data on highly polar compounds, which are key species in a much wider variety of industrial chemistries. This will facilitate our development of more accurate predictive methodologies, an area of vital importance as the pace of change outstrips our ability to provide information from a purely experimental standpoint.

Future Plans: The present work has demonstrated the power of providing the best possible data to American industry through a combined approach utilizing expert data evaluation, high-level calculations, and experimental measurements. In conjunction with other database work, we are continuing with the development of computational methodologies for the prediction of the physical properties of compounds. On the experimental side, we are undertaking kinetic measurements of species of great importance in soot formation and other concerns related to energy production.

Publication:

Manion, J.A., "*Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons*," J. Phys. Chem. Ref. Data (in press).

Phase Equilibria Measurements and Models for Hazardous Chemical and Mixed Waste Systems

CSTL Programs: Environmental Measurements, Physical Property Data

Authors: *L.A. Watts, C.D. Holcomb, and S.L. Outcalt*

Abstract: Mixtures of hazardous and low-level radioactive liquid wastes are in storage at Department of Energy (DoE) sites around the country. These hazardous chemical wastes contain many components in multiple phases, presenting very difficult handling and treatment problems. The safe handling, accurate characterization, and cost-effective design of new treatment techniques require an accurate and comprehensive knowledge of basic thermophysical property information, including the chemical composition and density of the phases. This project developed new modeling methods for these mixtures, and tested them with measurements made on a representative system (water + acetone + isopropyl alcohol + sodium nitrate). The model is based on the Peng-Robinson equation of state modified to include salts or other non-volatile components. The computer program written for the project predicts the vapor pressure, vapor composition, and phase densities, given the temperature and liquid phase composition.

Purpose: The purpose of this work was to perform measurements and develop models of a complex aqueous system for the Department of Energy (DoE). These studies are necessary for the safe handling and successful design of separation and treatment processes for certain hazardous chemical mixtures. These hazardous chemical wastes contain many components in multiple phases, presenting very difficult handling and treatment problems. The safe handling, accurate characterization, and cost-effective design of new treatment techniques require an accurate and comprehensive knowledge of basic thermophysical property information, including the chemical composition and density of the phases.

Major Accomplishments: Phase equilibrium and phase density measurements were performed for the representative system including water + acetone + isopropyl alcohol + sodium nitrate. These include studies of seven different mixtures in the past year, using an azeotropic VLE apparatus capable of making measurements at temperatures up to 425 K and pressures to 14 MPa. Additional measurements have been completed by collaborators at the Michigan Technological University, where studies of dilute systems were emphasized. A model was developed for mixed aqueous + organic solvent + salt systems using an equation of state model with mixing rules that allow the inclusion of a salt. The model is based on the Peng-Robinson equation-of-state (EOS) approach; this familiar EOS, commonly used in engineering applications, has been modified to allow the inclusion of salts or other non-volatile components in the system. The computer program written for the project predicts the vapor pressure, vapor composition, and phase densities, given the temperature and liquid phase composition. The model parameters are being optimized using the experimental results obtained at NIST and at MTU, as well as using other data available in the literature.

Impact: Mixtures of hazardous and low-level radioactive liquid wastes are in storage at Department of Energy (DoE) sites around the country. These measurements and models will be used by the DoE in modeling the tanks of water, solvents, and salts that are stored and treated at

the DoE facilities. The model also has the more general application to processes involving mixed solvent electrolytes, such as heat pumps, solvent extraction, and azeotropic distillation.

Future Plans: Continuation of the program is proposed to extend the components measured, to refine the model to include a group contribution method, and to develop a graphical user interface for the computer implementation of the model. The solvents added would be toluene, methyl ethyl ketone, 1,2-dichloroethane, and trichloroethylene, and the salt added would be sodium chloride.

Properties and Equations of State for Refrigerant Mixtures Near the Critical Point

CSTL Programs: Physical Property Data, Environmental Measurements

Authors: *M.O. McLinden, E.W. Lemmon, R.A. Perkins, A. Laesecke, and J. Magee; P. Domanski (863), and V. Payne (863)*

Abstract: The refrigerant blends now seeing commercial application as replacements for HCFC-22 in air-conditioning equipment can operate near the refrigerant critical point. This exacts a performance penalty, and understanding the causes is a high priority for the industry-sponsored 21-CR research program of the Air-Conditioning and Refrigeration Technology Institute. This project is supplying improved property data and models for the equipment testing and simulation work in BFRL. Measurements of heat capacity, density, viscosity, and thermal conductivity are included. It has also resulted in significant advances in our equation of state models and fitting procedures. These results will improve the accuracy of our refrigerant mixture models, which are transferred to industry primarily through the NIST REFPROP database.

Purpose: HCFC-22 is the refrigerant presently used in most residential and small commercial air-conditioners and heat pumps, but it must be phased out under international treaty. Refrigerant mixtures are the likely replacements, and systems using mixtures are now on the market. These blends, such as those with HFCs 32, 125, 134a, and/or 143a, have much lower critical temperatures than HCFC-22 and normally operate at considerably higher pressures. Under extreme conditions, the blends can operate near or above the refrigerant critical temperature and pressure, with major losses in capacity and efficiency. Understanding the causes of such losses is a high priority of the Air-Conditioning and Refrigeration Technology Institute's industry-sponsored 21-CR research program. This is a joint project with the Thermal Machinery Group of BFRL with funding from ARTI, the Department of Energy, and NIST.

There are very few property data for the blends near their critical temperatures, and the limited data at lower temperatures indicate that present mixture models are not adequate. There are strong indications that at least part of the observed deviations between the property model and experimental data are due to deficiencies in the pure-fluid R125 equation of state.

Major Accomplishments: We have completed measurements of the isochoric heat capacity of R125 at temperatures from 300 to 430 K, emphasizing states near critical, to complement our earlier measurements. The new measurements also yield pressure-density-temperature (P- ρ -T) data and have been used in developing an improved equation of state (EOS) for R125. This effort has advanced the state of the art in EOS fitting through a new equation form, a new nonlinear fitting method, and new constraints on the EOS parameters. These have yielded an equation with higher accuracy, fewer terms (i.e., faster calculation), better extrapolation behavior, and more theoretically correct behavior in the two-phase region, as compared to the previous EOS.

For the R410A blend, we have completed P- ρ -T measurements at temperatures up to 400 K, and we will measure the heat capacity of this blend as well. The available mixture data have been

used to develop a preliminary model for mixtures of HFCs. In developing this model, we are simultaneously fitting the pure fluid equations of state for R125, R32, and R134a, as well as the mixture parameters. The fitting algorithms have been modified so that the parameters for all three pure fluids as well as those for their mixtures are fitted simultaneously so that the best representation can be achieved for all the experimental data. Thus, the representation of the mixtures has been enhanced with the new pure fluid equations of state. This model will be finalized when all the mixture measurements have been completed.

The transport properties of viscosity and thermal conductivity are important in the analysis and simulation of heat exchangers, but data and models for the transport properties of refrigerant mixtures lag those for the thermodynamic properties. This project includes measurements of both properties for two blends. Viscosity measurements on HFC-32/125 and HFC-125/143a blends have been completed over the temperature range 300 to 420 K. The thermal conductivity of these blends will be measured in the coming year.

Impact: Increasingly, refrigeration systems are using refrigerant blends, and the new models being developed here will improve the accuracy of HFC mixture properties calculated with the NIST REFPROP database. The model will be applicable to ternary and higher order mixtures, without the need to fit additional parameters, and can be used with the present model for mixtures such as R125/R134a, etc. to allow a complete description of all refrigerant mixtures. The advances in equation-of-state modeling will enable us to deliver to our customers better equations for a wide range of fluids.

Future Plans: This specific project will be completed in FY2002. The remaining measurements will be completed and used in finalizing the equation-of-state models. The results will be incorporated into the NIST REFPROP database. The transport property measurements will serve as input to a separate modeling project beginning in FY 2002.